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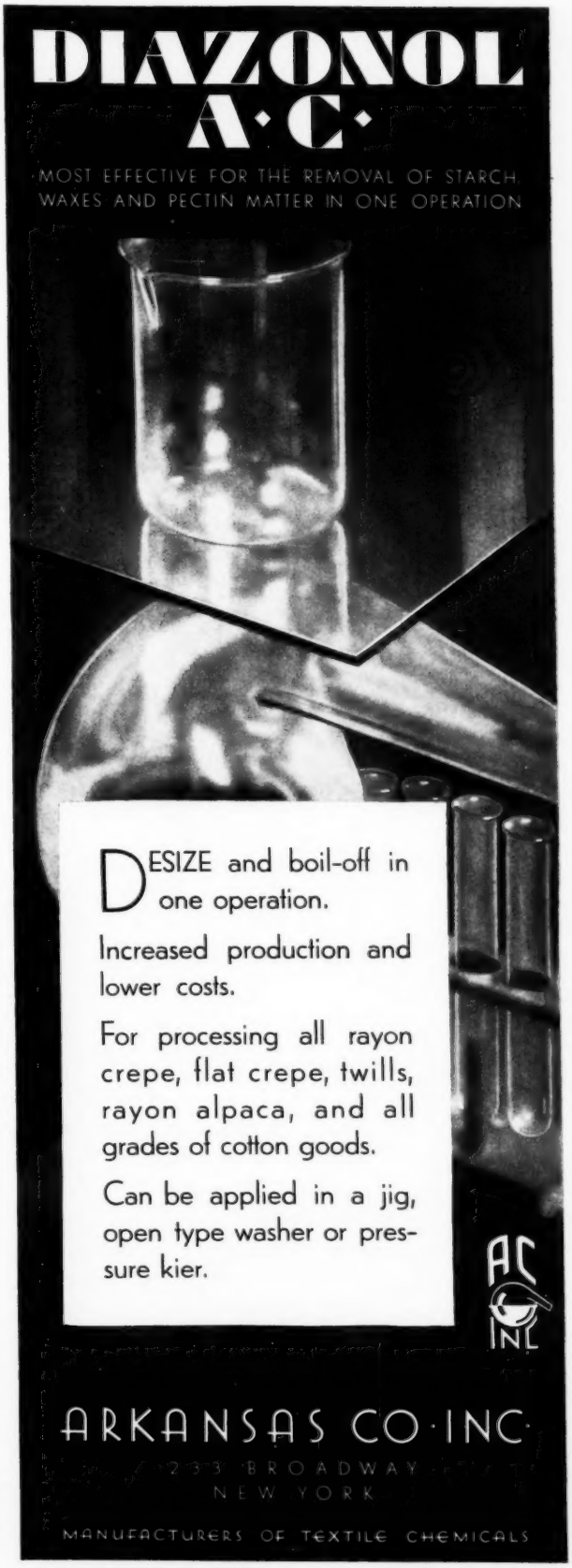
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Devoted to the practical application of dyestuffs in all industries; especially to textile chemistry—the science and practice of scouring, bleaching, dyeing and finishing.

Volume XX **MARCH 30, 1931** **Number 6**

Wool Oils

Basic Composition of Various Types of Wool Oils—Explanation of Their Ability to Form Emulsions—Consideration of Mineral Oil as a Component — Suggested Tests for Practical Evaluation

By **HENRY BARKER BURKE**

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WHEN wools of any kind are scoured and the proper rinsing has washed away all the soapy liquor, the natural oiliness of these wools has been removed. In order to secure the best results in the subsequent processes of carding and spinning it becomes necessary to add a suitable lubricant to this cleaned and dried stock. This added oil lubricates the fibers and protects the surface serrations of the fiber. It also renders the fibers more pliable and hence less susceptible to physical damage in these mechanical operations.

The essential function of a wool oil is to lubricate the stock in the mechanical operations of carding and spinning.

But positive lubrication at this point, important as it is, is but a minor consideration in the choice of a suitable wool oil, because it becomes at once, not alone desirable but absolutely imperative that the lubricant added can be easily and completely removed by normal procedure now common to the industry.

In like manner, a number of similarly important characteristics govern the proper choice of an oil. It must be free from gumminess or any tendency to harden. It must resist any tendency to decomposition or excessive oxidation. It should possess positive and uniform penetration when applied to various wool stocks. And, as the most approved means of application is in the form of an emulsion, the condition and stability of the emulsified oil should be given careful examination and be held under observation over a considerable period of time.

There seems to be a wide divergence of opinion concerning the use of mineral oils in the lubrication of wool stocks. Many notable and distinguished experimenters have condemned the use of a mineral oil, some holding that none should be employed in connection with wool oiling and some liberalizing to the extent of 30% mineral oil in a mixture with fatty oils. However, it is definitely known that the oil companies have for years been supplying both American and foreign mills with wool oils whose average mineral content is in excess of double the maximum amount of mineral oil suggested by or approved in text by the most liberal experimenters. And, moreover, these oils of high mineral content are daily in successful use in the most representative mills throughout the country.

The cost of a product (wool oil in this instance) is a matter of prime importance to any manufacturer and it must be economically adjusted to the grade of material being manufactured. The operation of wool oiling is in a large sense non-productive in that the oil is put on the stock to act as a lubricant after which it must be removed. It does not enhance the value of the product as does dyeing or finishing, and hence it follows that in the selection of a wool oil the optimum choice should be a product of the lowest possible cost that will satisfy a given manufacturing condition. However, the disadvantages from the use of a product of too low a quality should be guarded against.

In general there is a lack of fundamental knowledge concerning the indices which point to a "good" or a "bad" oil. It is widely known that a mineral oil will not emulsify with alkali (which fact, no doubt, caused many to hold mineral oil in abhorrence). But, a fact not so generally known is that vegetable or fatty oils without a free fatty acid content likewise will not emulsify with al-

kali. The emulsification by alkali is due to interaction with the free fatty acid producing soap in the surface layer. The addition of a small amount of free fatty acid to a mineral oil will render it emulsifiable with alkali. This may be accomplished, also, by direct addition of soap solution but in that case the emulsion is less complete and not so stable. In short, the surface layer of soap is produced more rapidly by the fatty acid in the oil and an alkaline solution than by actual absorption from the colloidal solution of soap. So, while the report on saponifiable and unsaponifiable matter in a wool oil sample is of importance by reason of placing the price range of the mixture, it cannot be considered as a basis for approval or rejection of the product.

In other words, should one through test discover or through report be informed that a certain submitted wool oil sample had, let us say, 70% unsaponifiable (mineral oil) matter present it would prove an error of judgment to reject this product as useless without further full and complete information concerning its other characteristics. No prejudice should be set up against mineral oil as such, for if it were possible to effectively remove mineral oils from stock by inexpensive means, then mineral oils without any compounding (added fats or soaps) would at once become the most proper recommendation for a wool lubricant. In some very few instances mineral oil is now used without any compounding but such cases are exceptions and we find that to use mineral oil with success it must be carefully compounded with fatty oils or other chemical combinations capable of effecting complete and stable emulsification.

The chemist besides determining the saponifiable and unsaponifiable matter in a sample very often checks the specific gravity, determines the saponification number and also the iodine number, checks on the color and the odor and likewise determines the free fatty acid content. From such an analysis one may identify the type of fat used as well as the proportions used. But such an examination has little value from a point of practical application of the product, but is, of course, important as a control in the maintaining of a satisfactory oil, or as a reference to the Purchasing Department in the establishment of a standard product.

Some have sought to purchase wool oils on the basis of time studied production tests against a standard product. For the most part such tests are not a measure of the oil in question, but are, in reality, a measure of the performance of the equipment, and the attentiveness and ability of the personnel. Products of doubtful value can be discovered by less expensive means and the small variation found to exist between various submitted samples in terms of pounds production or ends down or other similar counts will be found to exist in the selected oil when its day to day work is compared. The most that can be gained from such a test is the average performance of the oil.

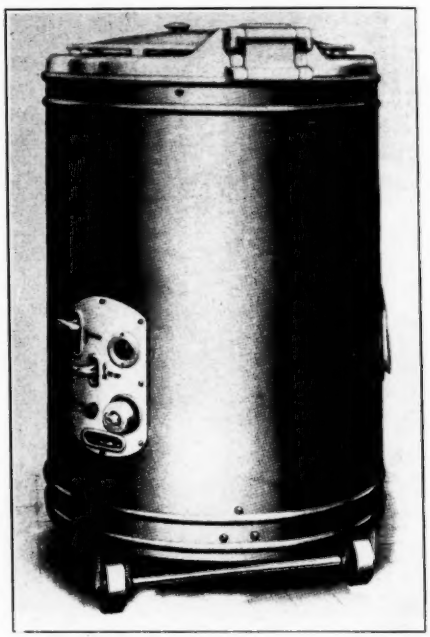
(Continued on page 224)

New Portable Extractor

The Textile Machine Works, Reading, Pennsylvania, has recently put on the market, The "Reading" Portable Centrifugal Extractor. This extractor with an outside diameter of 28", an overall height of 36" and weight of 480 pounds, has been developed with the principal aim in mind to produce a compact, high-speed, and efficient machine, designed along the most modern lines, and having a large range of uses.

The "Reading" extractor is built to carry a wet load of approximately forty pounds, and from four to six minutes are required for loading, extraction and unloading.

This extractor consists principally of a substantial cast iron base mounted on three rollers, Monel metal shell, eighteen-inch basket, centrifugal clutch, built-in mechanical brake, and driving motor.



The extractor basket, having an inside diameter of 18 inches, is of a new design, being a combination of a cast bronze center column and base, to which is attached a spun copper side and top. The holes in the side of the basket are drilled and countersunk and the inside finish is perfectly smooth.

Through the use of a centrifugal clutch, designed especially for this extractor, the motor shaft is gradually connected to the basket-driving spindle, thus insuring long life to the motor and the other driving parts.

The cover is of cast aluminum and has been designed to incorporate a safety mechanism that prevents the clutch from engaging until the cover has been closed and locks the cover in the closed position when the extractor is in operation.

Proceedings of the American Association of Textile Chemists and Colorists

The American Association of Textile Chemists and Colorists

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Edward W. Morgan, Chairman, Morgan Dyeing & Bleaching Co., Rochelle, Ill.
William Bergh, Jr., Secretary, Vassar Swiss Underwear Co., Chicago, Ill.

Lowell Textile Junior Section—
Alfred J. Carbone, Chairman; Paul Duggan, Secretary.

North Carolina State College Junior Section—
R. A. Gilliam, Chairman; D. B. Hardin, Secretary.

CALENDAR OF COMING EVENTS

Council and Research Committees—
April 17—New York.
May 15—Boston.

* * *

Annual Meeting
December 4, 5—Boston.

* * *

Exhibition of Color at the Museum of the Peaceful Arts, 220 East 42nd Street, New York. Starts January 2nd and continues several months.

* * *

New York Section Meetings—
April 24—New York.
May 22—Paterson.

* * *

Northern New England Section Meetings—
April 4.
May 2.

SIXTY-FOURTH MEETING RESEARCH COMMITTEE

THE Sixty-Fourth Meeting of the Research Committee of the American Association of Textile Chemists and Colorists was held at the Chemists' Club, New York, N. Y., Friday, February 27, 1931, at 2:45 P. M.

The following were present:

Chairman: Prof. L. A. Olney
Wm. D. Appel
J. R. Bonnar, representing A. E. Hirst
Harold D. Clayton
Ralph F. Culver
Dr. Carl Z. Draves
Walter C. Durfee
Ephraim Freedman
Robert H. Gaede
Walter E. Hadley
B. L. Hathorne
Ed. F. L. Lotte
Wm. R. Moorhouse
Dr. Hans Meyer
Dr. D. H. Powers
Dr. Robert E. Rose
Walter S. Williams
P. J. Wood
Secretary: Alex. Morrison

The Chairman announced that he had addressed letters to the various Chairmen of Sub-Committees asking for the status of the work of each Committee and outline of

work to be done by each this year and suggestions for future research in their particular line. He had received reports from most of these Sub-Committees. The various Chairmen present were asked to report their work and Prof. Olney reported for those not present from whom he had received letters.

Chairman Walter M. Scott reported for the Sub-Committee on Fastness Tests for Dyed Silk that the dyed silk standards were being checked up at the Bureau of Standards and that the Committee were going to consider whether or not another standard should be put in the line or a new substituted for one of the present ones. Otherwise work of this Committee is completed.

Chairman Hugh Christison of the Sub-Committee on Fastness Tests for Dyed Wool reported that their standard for washing fastness tests had been dyed on a semi-commercial scale and that samples had been distributed to several dyestuff concerns and several mills laboratories to be checked up before proceeding to dye up full length pieces. Work on Fulling Tests was still to be completed and it was hoped that Mr. William C. Smith, our Research Associate, would soon be released from present work in Washington to start more work on this line at the Lowell Textile Institute.

Chairman Olney reported for the Sub-Committee on Fastness Tests for Dyed Cotton that no definite report had been received. This work, however, is practically finished except for the dyeing of the standards in full pieces and which work the Committee was now considering having done. It was suggested that this committee consider dyeing their standards on a semi-commercial scale and having them tested before making full pieces.

Chairman Olney reported for the Sub-Committee on Light Fastness. The report of this Committee's recent work will appear in the Proceedings in about a month. This Committee is now studying and comparing the various types of fading lamps and is continuing the work of testing Dr. Krais test paper for determination of sun hours.

Chairman Hugh Christison of the Sub-Committee on Fastness to Perspiration reported that this work as published in the 1930 Year Book is completed unless criticism of those trying the tests demand a change.

Chairman Dr. Joseph F. X. Harold of the Sub-Committee on Methods of Testing Waterproof Textiles reported progress. A very lengthy and interesting discussion took place on several phases of this work.

The Sub-Committee on Vulcanized Rubber Fabrics had no report at this time.

Chairman Scott of the Sub-Committee on Color Standardization made an informal report on the Inter-Society Color Council which resulted from a Preliminary Conference on Organization of an Inter-Society Committee on Color Specifications, held under the auspices of the Optical Society of America in New York, February 26, 1930, and to which conference Dr. Scott, Dr. Draves, and Mr. Appel were our representatives. A formal report will be made at the next Council Meeting.

Chairman Olney reported on a letter from Russell W. Hook, Chairman of Sub-Committee on Standard Methods of Determining Sizing and Finishing Materials in Textile Fabrics. Methods proposed by this Committee are now being checked up in several different laboratories.

Chairman Howard D. Clayton of the Sub-Committee on Shrinkage of Textiles reported some progress, although his Committee hasn't done much to date. He made a request for methods of tests on shrinkage now in use in the trade that his Committee might consider them with ideas of theirs. Members are requested to communicate their tests to Mr. Clayton for his consideration.

B. L. Hathorne, Chairman of Sub-Committee on Rayon, reported very marked progress. He outlined the meeting of his Committee held the night before and certainly showed that his Committee was doing a very careful and thorough piece of work.

Dr. Carl Z. Draves, Chairman of Sub-Committee on Wetting Out Agents, reported that progress of the work of his Committee is held up until the publication of his article on Wetting Agents read at the last Annual Meeting. Members are requested to try out the procedure mentioned in this article and report their findings and criticism to Dr. Draves.

The meeting adjourned at 5:30 P. M.

Respectfully submitted,

ALEX. MORRISON,
Secretary.

FEBRUARY MEETING OF THE NORTHERN NEW ENGLAND SECTION

ON FEBRUARY 7th, in Cambridge, President Wood was the guest of the Northern New England Section, addressing the meeting and conferring with the sectional committee with regard to the next annual meeting, to be held in Boston on December 4th and 5th. Harry R. Davies was chosen by the section to head the committee on general arrangements.

Eskel Nordell of the Permutit Co. spoke on "Treatment of Water for the Textile Plant." There were present about fifty, of whom thirty-nine attended the dinner. At the next meeting, on March 7th, Chester C. Stewart will speak on "Automatic Temperature Control in the Textile Industry."

Respectfully sumbitted,

HAROLD C. CHAPIN, *Secretary.*

Address of P. J. Wood, President of the Association, Before the Northern New England Section

MR. CHAIRMAN, Gentlemen: When my friend Mr. Zillesson rang me up a little while ago, and asked me to come up here on a Saturday. I looked up my calendar and found that this was the only night I would be at home. I couldn't say "No." Particularly as I was desirous of seeing the Boston Section during my year of office. I assure you, however, that if I am lacking in your opinion in any respect, it is because I feel tired after a very strenuous week. The other day, after looking over an issue of "Life," I saw a verse. If it hadn't been for one wicked word in it, I might have thought it had been written by my wife. It went like this—

> The cricket is on the hearth, dear,
> Here is your pipe and a book that is new.
> Your slippers are by the fire, dear,
> But where the hell are you.

Having to make a visit to all the sections during my term of office, I am afraid my marital relations are about to be strained. But, I have had these bad habits some years now, and I think we are getting adjusted. I feel something like the Governor of New York addressing the prisoners of Sing Sing. He started by saying "Gentlemen!" then he decided that that was not the right word, so he started again, "Fellow citizens!" and then he remembered that most of them had been disfranchised. So, he started again. "Fellow Prisoners! and finally giving it up as a bad job—Well, anyway, I'm glad to see so many of you here." That is the way I feel to-night—glad to see so many here. When I asked Mr. Grimes what he would like to have me talk about, he said "Anything." So, that is what I am going to do, talk about anything.

In visiting the different sections, I like to find out just about how they run their sections in order to pass along the best of their methods to other sections as I visit them in turn. And, it might interest you to know something of some of the sections with which I have come in contact. I was looking over your calendar of the meeting, and immediately something struck me about it that has struck the committee in our section, and that was this. That you start out by announcing that there will be a dinner at such an hour, price $2.00. Some readers would immediately say, "I haven't the two." (The Scotch ones possibly). Then you announce the meeting below, the time of the meeting and the speaker. In the New York Section, we have reversed that, and we make the meeting announcement of primary importance, and the dinner incidental. We have a good attendance and I think that is a little point you might try. I've heard you don't have quite the attendance you'd like to have and that might help. Discussing that point with the Philadelphia Section, they told me that if they had the meeting in a room other than the dining room, their attendance was improved. This is because the men who don't care to come to the dinner, and who do like to come to the meeting would then come and they wouldn't feel if they were to meet in the room in which you have had your dinner. I leave that for your consideration. The success of a section whilst it doesn't depend on numbers depends on growth, because people like to belong to a live organization. I do and you do. Everybody likes to be associated with success, and growth, however small, means success. For that reason, an active membership committee should be a part of every section of our association. You have such a membership committee and probably they are functioning the way they should. You know, I don't. We have found that in New York we have had varying results. We found that the year when we had the peppiest membership committee we had the largest growth. But, this work does not depend only on the membership committee. There might well be a committee of the whole, if each member of the section would constitute himself a member of that imaginary committee and think of all the people who should belong to our association but who do not. We have about 1350 members and should have twice as many. There are more Textile Chemists in the United States by far. There are a great many people interested in our work who would like to come to some of our meetings or all of them, and would like to meet our members. Many of them could become associate members. We have several in the New York Section. So, there is another thought you have to consider—for each man to consider, not only your officers. All of you can be salesmen for your Association. Be bold, don't give up. The success of the Association depends on the effort of every one of us. It is up to us to bring to it the best kind of material. The more members we have, the more in common the Association has, and I think it can be said without fear of contradiction that our Association has done more research work than any other Association in the United States—under the able leadership of Prof. Olney. He has carried out a wonderful work with his large committee. They have co-operated splendidly. The funds have been limited and this work can be extended if the necessary funds are forthcoming. By increasing the membership, we can increase the funds for this purpose. Now, there are other things about this work that might be touched upon although they are not very important ones. One

is to choose the best time for meetings. There are all kinds of conditions in the different sections. I found that the Piedmont Section had meetings in different towns, generally Charlotte and one other place. We follow the same plan in New York. We have a great many members on both sides of the Hudson. We meet in New York, and of course, we have many Jersey members who go over there to those meetings, and then, the alternate meetings we hold in Paterson. We found that a very good plan. The Piedmont Section meets only once in three months. I have been to only one of their meetings. I attended it some years ago, and they make a field day of it. They take their wives and children along and have swimming, golf, etc., then they have the meeting in the evening. We have one in the New York Section once a year. We don't combine that with any business at all. We have an annual meeting just one meeting before that, in which we elect officers. One thing that we tried in the New York Section which, however, did not work out very well, we tried it for one season—that was the question box. It occurred to some of us that there were people who would like to ask questions. Some of the older members so frequently had questions asked by some of the younger members that we thought of the question box. We had probably three of four questions at a meeting. Then, we invited the members present to answer the questions. Some were trade secrets, or so regarded. But it was surprising what a great deal of information and what helpful discussion was aroused by the question box. I leave that also for your further consideration. The program of speakers is, of course, the main concern of your Sectional officers and program committee; but here again the rank and file of the membership of your Section can be very helpful by suggesting speakers with whom the program committee may communicate, or by themselves approaching interesting speakers and inducing them to give their service as speakers. This is my first appearance to be able to thank you for the National Office I hold. I am very glad to serve and I know that the National Officers will have the support of the New England Section along with the other sections of the Country. I am glad to be here with you tonight and to know you.

Statement of Louis A. Olney, Chairman of Research Committee

UPON the request of Chairman Grimes, Prof. Olney made a brief statement to the Northern New England Section in regard to the co-operative work of the U. S. Institute for Textile Research and our own research committee. He spoke as follows:

Reference has been made to the United States Institute of Textile Research and it has been suggested that I give you some information in regard to this newly formed body.

Several years ago an organization known as the Textile Research Council was formed by some fifteen of twenty American members of the British Textile Institute. The object of this Textile Research Council was to encourage textile research in the United States. Later this organization became one of a more general character and took in as members anyone interested in textile research, whether they were members of the British Association or not.

The American Association of Textile Chemists and Colorists particularly through the Research Committee was quite closely associated with the Textile Research Council as a large proportion of the members of this Textile Research Council were also members of your Association.

When the Textile Foundation was constituted by vote of Congress a few months ago with an annual income of between forty and fifty thousand dollars a year, to spend upon research related to textiles and allied subjects, the whole matter of suitable agencies to carry out this work was discussed in a joint meeting of the two bodies. As a result of deliberations on the part of the officers of these organizations, many of whom were prominently connected with both bodies, it was finally decided and voted that the general interest of the textile and color industry would be best served by the formation of an entirely new organization. As a result the United States Institute for Textile Research came into existence and the Textile Research Council was later dissolved. It is the hope of all concerned that the United States Institute of Textile Research may eventually develop into a sufficiently well endowed institution to carry on textile research in this country and be comparable with that of the British Textile Institute and its allied organizations. It is expected that the United States Institute for Textile Research will work very largely through the Research Committee of our own association as far as its work in relation to textile chemistry, bleaching, dyeing, printing and finishing is concerned, and as it develops and becomes of a more mature character will be able to assist financially in the support of our work.

Naturally at the time of its organization the United States Institute had practically no funds and in order to indicate in a substantial manner our spirit of co-operation we voted at the Annual Meeting in Chattanooga to take out a life membership and in this way contribute $1000 towards the permanent funds of the institute and also for one year a contributing

membership of one hundred dollars in order to assist in the organization work.

Annual Memberships in this association are $10.00 a year and I wish to take this opportunity to suggest that as many members of the A.A.T.C.C. as may be able take out an annual membership, and in this way help to assure the future of textile research in the United States. In this way also, we believe that you will help assure the future of the research work of our own Association, because as the former grows and its financial resources increase we confidently believe that we may eventually receive material support from them for our work.

The fact which I believe above all others will interest you at the present time is that the Textile Foundation, already referred to, has voted $5000.00 for the use of our Research Committee during the coming year. It is the intention to spend practically the entire amount in securing additional full time research associates. This is the kind of recognition for which we have been working and looking forward to for a number of years and we hope that this may be the beginning of a far more extensive and useful existence of the Research Committee of our Association.

A New Method for the Evaluation of Wetting Agents*

By Dr. Carl Z. Draves and Dr. R. G. Clarkson
E. I. du Pont de Nemours & Co., Inc.

THE textile industry, as you have been told so often by others, offers many problems to the colloid chemist. Most of the processes in printing, dyeing and finishing involve colloidal phenomena and most of the chemicals employed are colloidal in their nature. Colloidal materials are surface active and it is because they act on surfaces that colloidal materials are of such interest to the textile chemist. Some of the colloidal products used widely in the textile industry are the following: detergents, emulsifying agents, wetting agents, dyestuffs, dispersing agents, retarding agents for dyeing, protective agents for dyeing animal fibers with sulfur and vat colors, starches, gums and many other things.

Each one of these classes of materials, or chemical agents, could be made the subject for any number of fundamental researches and papers. We mention them, however, merely to introduce the topic which is about to be discussed, namely, wetting agents, because wetting agents also are of value for their surface activity.

*Presented at the Annual Meeting.

If we consider some of these classes of colloidal materials for just a moment in a general way, we must realize that much work has already been done in attempting to understand the principles of their action and in devising and perfecting practical tests for their efficiency. For example, many physical chemists have investigated the behavior of soap solutions and other detergents. And yet, there is still need for a really satisfactory laboratory test by which practical detergent ability can be measured. Our own Bureau of Standards and other laboratories are working on that problem at the present time. Detergent ability and ability to act as an emulsifying agent both seem to be connected with surface activity.

Although "dispersing agents" and "dispersion" are terms so often employed by dyers and printers, the test introduced by Zsigmondy of measuring the efficiency of a dispersing agent by a determination of its gold number has probably never been employed in the American textile industry. Such substances as glue, gelatin, starches, gums and some aromatic compounds are dispersing agents; they act as protective colloids; that is, they tend to prevent the aggregation of hydrophobic colloidal particles. There are a few chemists who hold a wrong conception with regard to the action of dispersing agents since they believe that a dispersing agent is able to cut the original solid discrete particles of a suspension into smaller pieces, as if by a knife.

There is another class of surface active substances, retarding agents for dyeing, about which we have little real knowledge. Probably great profit would result from thorough studies of the effect of different substances on dyeing rates. For the dyeing of vat colors in circulating machines nothing seems more efficient than ordinary glue; but the fault with glue is that it holds the dye off at the end of the dyeing as well as at the beginning. Something is needed which will be as efficient as glue, or more so, the first five minutes of dyeing and then will decompose rapidly or become innocuous, for it can easily be shown that when there is good contact between dye solution and fiber, half of the dye exhausts in a very short time.

Textile colorists are, of course, most interested in the surface active substances which we call dyes. The subject of dyeing has received much attention, both on the practical and the theoretical side. Dyeing as an art is fairly well advanced and the methods for testing dyestuffs are quite satisfactory because the results are evident by visual examination.

Wetting Agents—Previous Work

Artificial wetting agents are surface active materials which have been in use for a much shorter time than the other surface active agents which we have briefly discussed. As a consequence, it would be expected that not only is the art of using wetting agents not yet well

advanced but also satisfactory practical methods for testing the efficiency of wetting agents have not been available.

There is no need for us to review the work which has already been done in the field of testing wetting efficiency because that has been satisfactorily recorded by others. We may list a few of the more important articles, however, which will give the interested reader a complete history of the subject:

1. J. Auerbach, Textilberichte 7, 681 (1926).
2. A. J. Hall, J. Soc. Dyers & Colourists 1, (1930).
3. Herbig & Seyforth, Textilberichte 8, 45 and 149 (1927).
4. W. Kind & J. Auerbach, Textilberichte 9, 775 (1926).
5. Lachman, Textilberichte 7, 851 (1926).
6. Landolt, Melliand 1, 96 and 243 (1929).
7. W. H. Nuttall, J. Soc. Dyers & Colourists 40, 104 (1924).
8. A. Ruperti, Textilberichte 7, 936 (1926).

None of the methods which have been proposed for testing the efficiency of wetting agents for textile fibers have been satisfactory. The greatest criticism to be made, however, of the work of those who have published data with regard to the relative efficiencies of wetting agents is that they have not emphasized well enough that those quantities of wetting agents are equivalent under the conditions of testing, which *cause the SAME RATE of wetting*. Landolt (6) suggested that equivalent quantities of wetting agents on a price basis be tested, but, as we shall show later, such a test will indicate only which is better at the price, and not how much better one is than the other.

The New Method

In 1926 one of us devised a method for the evaluation of wetting agents which has given very satisfactory results in our laboratory since that time. The method, briefly, consists of measuring the time required for a 5 gram unboiled skein of gray 2-ply cotton yarn to sink in a solution of the wetting agent, when the skein carrying a 1½ gram sinker is held below the surface of the wetting solution by a heavier weight called the anchor.

The sinker and anchor (see Fig. 1) are prepared as follows: The sinker, "a and b," consists of a short length of copper wire, "a," just long enough to go around a 5-gram skein and to be fastened by hooking the ends of the wire together, the ends having been bent so as to hook easily. To the middle of the copper wire is fastened a small lead weight, "b." The combined mass of the copper wire hook and lead weight, which together constitute the sinker, is adjusted to exactly 1½ grams by carefully shaving off excess lead from the lead weight. The sinker is fastened by means of a strong but fine mercerized cotton thread, "c," to the anchor, "d," which

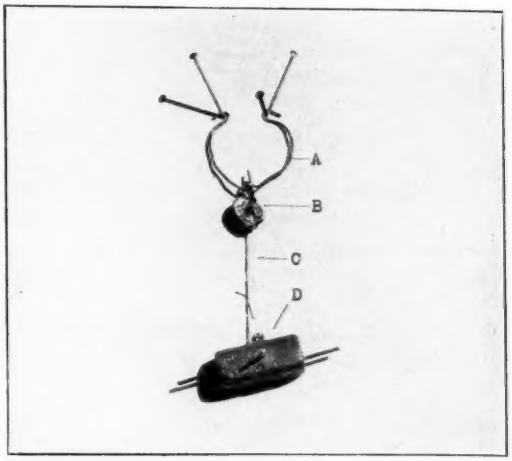

Fig. 1.

should weigh at least 20 grams. The sinker and anchor should be 1 inch (25 mm.) apart. The anchor may be of lead with a small staple driven into the top in which to fasten the thread. Pins may be driven into the anchor in a horizontal plane, one on each side, and the heads cut off. They serve to keep the anchor centered when in use.

For a determination, a five gram skein is folded once so as to be formed into a loop half as long as the length when extended. The sinker with its anchor is fastened at one end of the doubled skein and the skein is cut through with shears at the end opposite the sinker. The cut end of the doubled skein is grasped with the hand—the operator should be careful to leave the cut ends of the yarn open and loose—and the skein, with the sinker and anchor dangling at the bottom, is dropped into the solution of the wetting agent contained in a 500 cc. graduated cylinder. The time elapsing between the entering of the skein and the moment when the weighted skein starts to sink is measured with a stop watch. The skein before sinking must be entirely covered with the solution and yet must possess enough buoyancy from the entrapped and adsorped air to keep the thread between the anchor and sinker taut. (See Fig. 2.) The average of at least four determinations of sinking time should be obtained for each concentration of wetting agent.

Dr. K. P. Munroe (unpublished work) determined that a 5-gram cotton skein entrains about 15 cc. of air which escapes when the skein becomes completely wet out. In our test, the air escapes rapidly from a skein in a wetting solution until the buoyancy becomes decreased sufficiently for the skein to sink. In plain water, on the other hand, a skein hardly gives up any air at all and will not sink with the 1½ gram sinker even after several days' immersion. Munroe also found that the presence

Fig. 2.

of adsorbed air has little to do with the readiness with which cotton wets out in a Nekal solution. A cotton skein, from which air had been practically completely freed from air by the passage of dry ammonia gas over it for 3 hours, wet out in a Nekal solution in about the same time as one which had not been so treated.

In testing a wetting agent it is convenient to prepare a stock solution containing 100 grams of wetting agent per liter of solution. The following sized aliquot portions, diluted to 500 cc. in a volumetric flask, are used for the determination of sinking times: 5, 10, 25, 35, 50, 75, and 100 cc., corresponding respectively to 1, 2, 5, 7, 10, 15, and 20 grams per liter. This range of concentrations covers the measurable sinking times for practically all wetting agents.

It is to be assumed that ordinary quantitative technique is employed in the preparation and dilution of solutions. The wetting agent should be well dissolved—heated somewhat if necessary—and then diluted to the liter mark with cold water. An aliquot portion of this stock solution is withdrawn with a bulb pipet and is diluted to 500 cc. in a volumetric flask. Mixing of this solution is obtained by pouring it from the flask into a liter beaker and from the beaker directly into the 500 cc. graduated cylinder. To obtain concordant results, it is important to wait a uniform length of time after the wetting solution has been poured into the cylinder before entering the weighted skein. We have always waited 45 seconds because in that time the sinker can be attached to a skein and the skein can be made ready for the test. The ideal condition would probably be to wait sufficiently long to allow the foam to subside completely.

In the determination of sinking times it is necessary to use a fixed temperature. We have found it most convenient the year round to use 25° C. (77° F.), attaining that temperature with sufficient accuracy merely by using water for dilution from a large pail or pot which has been heated or cooled to 25° C. For tests at higher temperatures we have used water for dilution which had been heated several degrees warmer than the temperature desired. The solution in the cylinder could then be cooled if necessary by standing the cylinder for just a moment in cold water.

The method of handling the data obtained by the methods described above is very important. Points are plotted on log-log coordinate paper, distances along the abscissa representing the logarithms of the numbers of grams of wetting agent per liter and distances along the ordinate the logarithms of the average time of sinking in seconds. A smooth curve is drawn through the points. (See Fig. 3.)

Since solutions which cause sinking of the skeins in equal times under similar conditions must be equivalent in wetting ability, equivalent quantities of wetting agents are readily obtained by reading from the curves the concentrations which cause sinking in a certain arbitrary time. For our work we have chosen a sinking time of 25 seconds for comparison because the corresponding concentration (2.5 to 4.0 grams per liter for the better commercial products) comes within the range which is employed for practical work. For example, if 4 grams of one agent is required to cause sinking in 25 seconds and 5 grams of another, the second is only 80% as effective as the first. The selling prices, to be competitive, should reflect the same difference as the difference in wetting efficiency.

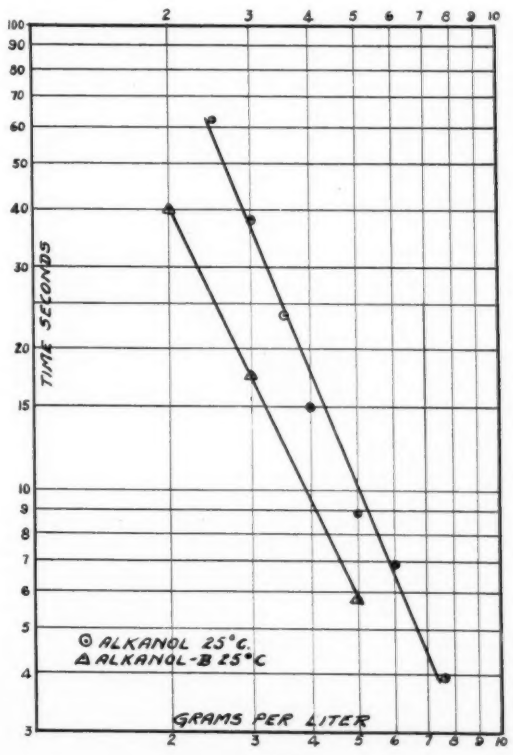

Fig. 3

A Study of the Method

When the method under consideration was first devised, it was necessary to determine the most suitable weight for the sinker. We shall not stop here, however, to go into detail with regard to those experiments since it is probable that this work will be reported later more completely in another journal. In any event, it was found that a 1½ gram sinker gave the most reliable results. With no sinker the results were very erratic, indeed; with a 2½ gram sinker the sinking times were too short. This study also showed that the per cent error in the amount of wetting agent to cause sinking in 25 seconds was much less than the per cent error in the weight of the sinker. From this fact it can be logically inferred that errors in the weights of the skeins employed or differences in the specific gravities of the wetting solutions have smaller effects on the accuracy of the determination than would be supposed.

Value of the Method

The new method for the evaluation of wetting agents is of value both to the manufacturer of wetting agents and to the textile industry. By use of the method, the manufacturer of wetting agents is enabled to turn out a uniform product, the purchaser to choose the brand which gives the best money value, and the man in the mill to employ wetting agents under the most favorable conditions. That the conditions of wetting are of greater importance than some realize is given by the example of the effect of temperature; turkey red oil is a wetting agent below 60° C. (140° F.) but above that temperature it is not a wetting agent at all.

The study of the conditions affecting wetting has not only proven of great practical value but also of considerable theoretical interest. By the new test, the conditions affecting wetting can be studied, both theoretically and practically, with solutions which exactly duplicate those which may be employed in the mill. The factors affecting wetting which have been investigated are the following: 1. Concentration of wetting agent; 2, temperature; 3. pH; 4. concentration and character of crystalloidal substances (acids, bases and salts which are not colloidal in nature) present with the wetting agent; 5. concentration and character of other colloidal or surface active materials present, and 6, the history of the wetting solution.

As we might very well expect, the behavior of wetting agents under different conditions can be pretty well anticipated from a general knowledge of the effect of colloidal materials on surface tension. Probably the best source of information concerning surface active substances and surface tension is Freundlich's "Kapillarchemie." It has been assumed by most people — though some have denied it—that wetting efficiency and surface tension are related. Up to the present time, however, it has never been clearly proven that there is a definite and regular relationship between these properties.

Concentration, Surface Tension and Sinking Time

The first condition affecting wetting which received our attention was that of concentration of wetting agent. Although the new method of testing is entirely empirical in that sinking times are relative and have no theoretical foundation, it is remarkable that when sinking times and the corresponding concentrations are plotted on log-log coordinate paper, straight lines are obtained for the alkylnaphthalenesulfonic acid, alcohol and some other types of wetting agents. The relation of sinking time to concentration for these types, therefore, can be expressed by the simple equation, $\log t = s \log c + b$, where t and c represent average sinking time in seconds and concentration in grams per liter, respectively, and s and b are constants. Each type of wetting agent gives a curve with its own characteristic slope.

TABLE I.

Wetting Agent	Sinking Time	Surface Tension
g per l	Seconds	Dynes /cm
Alkanol		
0.0	—	72 4
5	—	52 6
1.0	—	48 9
1.5	—	46 7
2.0	135	45 4
2.5	62 1	42 5
3.0	37 7	41 9
3.5	23 5	40 4
4.0	15 0	38 5
5.0	8 9	37 5
6.0	6 9	37 2
7.5	3 9	36 4
10.0	1 0	37 3
50.0	0 0	36 4
Alkanol B		
2.0	40.0	
3.0	17.3	
5.0	5.7	

Temperature 25° C (77°F)

A consideration of the fact that the relation between sinking time and concentration is logarithmic makes clear why it is so wrong to assume that one wetting agent is twice as effective as another if it causes wetting in half the time. Also, because of this logarithmic relation, an average deviation of 10 per cent in successive determinations of sinking time does not at all mean an average deviation of 10 per cent in the value of the concentration which causes sinking in 25 seconds. As a matter of fact, when the slope of the wetting curve is like that of Alkanol in Fig. 3, an average deviation of sinking time of 10

per cent corresponds to an average deviation of only 4 per cent in the value of the concentration to cause sinking in 25 seconds. If four trials are made for each concentration, the accuracy of the final value, therefore, is 4 per cent divided by the square root of the number of trials, or 2 per cent. Our experience with Alkanol has shown that successive determinations can be made several months apart with a stoppered sample of wetting agent using skeins from entirely different lots of yarn with an accuracy which does correspond to an average deviation of about 2 per cent in the value of the concentration to cause sinking in 25 seconds.

In arriving at an average value for the sinking time for a given concentration, the beginner must resist the temptation to reject any single sinking time which seems too far variant, unless the deviation of that value from the mean of the other three is more than four times the average deviation of those three. It will be found that under ordinary circumstances, if this rule is followed, the results from sinking trials will only occasionally need to be rejected.

The figures for surface tension given in Table I show clearly that the efficiency of a wetting agent is very certainly dependent upon its capacity for lowering surface tension. Measurable sinking times by the new method were obtained when the surface tension of various solutions tested, including Alkanol, Nekal A and BX, Neomerpin S A Conc., Merpentine, turkey red oil, soap, and alcohol, was from 45 to 35 dynes per centimeter. Below 35 dynes the skeins sank at once. For the alkylnapthalenesulfonic acids and alcohol it was found that the lowering of surface tension was directly proportional to the logarithm of the concentration. Freundlich's Kapillarchemie, already referred to, contains considerable discussion concerning this relation between lowering of surface tension and concentration. In an article by Woodman upon the subject of "Wetters and Spreaders" are given surface tension values for some common substances in solution.

(9) Woodman, Chemistry and Industry 49, 96 T (1930).

Surface tension measurements in our work were made by the ring method with a du Nouy Tensiometer because by that method approximate results could be obtained so quickly and simply. Although the values were only approximate, they served to prove conclusively the general relation between wetting efficiency and lowering of surface tension, and they also showed the range in lowering of surface tension which is necessary for wetting unboiled cotton in a reasonable time. For the errors of the du Nouy ring method when applied to a colloidal system see (10) J. Biol. Chem. 84, 543 (1929).

Although our work proves conclusively that wetting efficiency is a function of surface tension, it was not sufficiently accurate to prove whether or not two solutions exactly equivalent in wetting power for cotton possess equal static surface tensions. In fact, it will be necessary to determine static surface tensions much more accurately to prove this point. Yet it must be pointed out that within about one dyne, that is within the accuracy of our determinations, wetting power *was* proportional to the lowering of static surface tension. Since new surfaces are formed when cotton is immersed in a wetting solution, however, it is very probable that the rate of wetting is dependent, to a very slight extent, upon the initial dynamic value for surface tension and upon the rate at which the static surface tension is attained as well as upon the final value of the static surface tension. The rate at which a new surface in a colloidal solution attains a static surface tension is generally accepted as being determined by the rate at which solute molecules can diffuse from within the body of the liquid and be absorbed into the new surface. The new method of testing wetting rate might prove of some value in solving these theoretical questions with regard to the mechanism of the wetting of cotton.

Foaming

Since the tendency of a liquid to foam is dependent upon its surface tension, it is appropriate at this point to discuss the subject of foaming for a moment in connection with wetting agents. As clearly reviewed by Freundlich, a considerable foam can be induced in a liquid by agitation only when both the surface tension and the vapor pressure are low. Both these conditions are fulfilled by solutions of the artificial wetting agents. The lower the surface tension of a solution, the greater is the tendency to foam and also the greater is the wetting power. Because surface tension acts in such a way that the total surface of a system tends to attain a minimum, the foam on the surface of an artificial wetting agent slowly subsides after agitation ceases, even though the value of the surface tension is low. Soap froths, on the other hand, tend to be much more stable because a semi-rigid gel is formed in each lamella of the froth. It is both interesting and practical to know that for years chemists have employed the device of making a froth on an aqueous solution subside more quickly by adding an easily volatile, light, immiscible liquid, such as ether, turpentine, or pine oil. Although it must be accepted as a fact that solutions of wetting agents foam, they are valuable for the prevention of so-called foam specks in vat dyeing because they cause any oxidized pigment which floats on the surface to wet, sink and re-reduce.

Temperature and Wetting

Different types of wetting agents behave very differently in the effect of temperature on the rate of wetting. The alkylnaphthalenesulfonic acid types of wetting agent gave a series of approximately parallel lines for log concentration—log sinking time curves. At 60°C (140°F) it required 4.1 grams of a certain sample of Alkanol to

cause sinking in 25 seconds, whereas, at 25°C (77°F), it required 3.3 grams per liter. At 85°C, Alkanol was only about half as effective as it was at 25°C. Soap, on the other hand, generally speaking, was more effective as a wetting agent when hot. The log concentration and log time curves for soap, however, are so peculiarly shaped, not being straight lines but always showing minima, that the behavior of soap as a wetting agent is a subject in itself. The wetting efficiency of turkey red oil in the presence of soda ash was so adversely affected by rise in temperature that at 60°C (140°F) it ceased to be a wetting agent at all. At that temperature, it may still act as a detergent, but it does not have wetting properties.

When an increase of temperature decreases the wetting efficiency of a wetting agent, it probably does so by increasing the average dispersity of the colloidal solution, making the agent less surface active and more crystalloidal in properties. Soap, on the other hand, becomes a better wetting agent at higher temperatures because a greater portion of the complex micellae break up and become surface active, thereby reducing surface tension more than at lower temperatures.

pH and Wetting Efficiency

When we came to study the effect of variations in pH on wetting efficiency, we found that a change in pH had much more effect on some wetting agents than on others. The wetting efficiency of turkey red oil was practically doubled by the addition of just enough alkali to give a clear solution; more alkali had but little effect. The wetting curves for soap were so complicated that it is rather hard to generalize in a few words with regard to the effect of alkali on soap. The addition of an equal quantity of soda ash to soap made the soap only 1/3 as effective at 60°C as it was at that same temperature without soda ash. This effect of soda ash on soap was probably due as much to a salting out tendency as to a pH effect. The addition of acid to soap and sulfonated oil to attain pH values less than 7 simply caused these agents to lose their wetting power entirely due to separation of the free acid.

The artificial wetting agents, on the other hand, behaved very differently with changes in pH than soap and turkey red oil. A series of solutions of Alkanol was prepared, each solution containing 5 grams of Alkanol per liter and increasing amounts of caustic soda. Sinking tests with these solutions showed that at 25°C the wetting efficiency gradually decreased with increase in alkalinity until at pH 12.5 the wetting efficiency was 30 per cent less than at pH 7.0. From pH 12.5 to 13.0, there was a sharp increase in wetting efficiency from 30 per cent to 40 per cent greater than the efficiency of a neutral solution. At pH values above 13.0, the wetting efficiency decreased very rapidly, due to salting out of the wetting agent. From these results we can understand why Alkanol is very suitable for use in alkaline kier boiling liquors and in other situations where the pH is 13.0 or below, but is not suitable in mercerizing liquors where the pH is considerably above 13.0.

Sinking experiments were also performed on the acid side of neutrality with Alkanol using increasing concentrations of sulfuric acid with 3.3 grams of Alkanol per liter. The sinking time decreased regularly with decrease in pH from 25 seconds at a pH value of 7.0 to 9 seconds at a pH value of 1.1 (pH values were determined with a comparator). This decrease in sinking time corresponded to an increase of 30 per cent in efficiency in the most acid solution. In a carbonizing bath, therefore, the alkylnaphthalenesulfonic acid type of wetting agent can be advantageously employed to cause the acid to wet the cellulosic materials present in wool and to react more readily with them.

Salts and Wetting Efficiency

The addition of salt to pure water causes a rise of surface tension. When salt is added to a solution of Alkanol, Neomerpin SA Conc., or Nekal, on the other hand, the surface tension of the wetting solution is lowered still farther and the wetting efficiency is increased. This behavior, which has been noted in the folders descriptive of the three products listed above, is consistent with the effect of salt in general on surface active colloids. 25g of purified salt per liter increased the wetting efficiency of a 2g per liter solution of Alkanol B by 58 per cent, or, in other words, it decreased the sinking time at 25°C from 77 seconds to 21 seconds. Concentrations of salt above 25 g per liter, however, were less effective than 25g in increasing the efficiency of a 2 gram per liter solution of Alkanol B until at 50 g per liter of salt the wetting agent became less effective than without salt. Concentrations of salt above that which caused the greatest increase in wetting power gradually brought about a salting out of the wetting agent with a consequent gradual loss in wetting efficiency. Since it required some time for the process of salting out to go to completion, concordant results were obtained for high concentrations of salt only by adhering strictly to a wait of 45 seconds after preparing the solution for test.

One should expect that salts furnishing *bivalent* positive ions would have more effect on wetting agents than equivalent concentrations of salts furnishing monovalent ions, because wetting agents exist in solution as negative colloids. Such indeed was found to be the case. 0.875 g of calcium chloride per liter increased the efficiency of a 3 gram per liter solution of Alkanol B by approximately 25 per cent. Concentrations above 0.875 g of calcium chloride per liter, however, had the same effect at 25°C as concentrations of common salt above 25 g per liter, that is, they tended to throw the wetting agent out of solution. With concentrations of calcium chloride below 0.875 g, on the other hand, the Alkanol hardly tended to go out of solution in the slightest degree. Proof of

this conclusion is furnished by the fact that the sinking time did not increase appreciably and gradually with standing after the addition of the calcium chloride. For example, the average sinking time for 3g of Alkanol B in the presence of 0.70 g. of calcium chloride per liter was 14 seconds when measured 45 seconds after mixing and 15½ seconds when measured 30 minutes after mixing. The difference between 14 and 15½ seconds was hardly significant. These experiments on the effect of bivalent ions on the wetting efficiency and the solubility of artificial wetting agents verified the observations found in several places in the literature that hard water increases the wetting efficiency of the salts of the alkylnaphthalenesulfonic acids. It is evident also from the concentration of calcium chloride which was found necessary to throw this type of wetting agent out of solution that Alkanol or Alkanol B can be employed in water which contains more calcium than any naturally occurring hard water.

Effect of Other Colloids

Glue and Bindex, although they do lower surface tension somewhat as do most colloidal solutions, nevertheless are not wetting agents. It might be expected, however, that they would have an effect on the efficiency of wetting agents. But it was found that the effect of even rather high concentrations of either of these substances was not so very great. 5 grams of animal glue per liter increased the sinking time of a 5 gram Alkanol solution from 7 seconds to 13½ seconds. 2.5 grams of Bindex per liter, on the other hand, decreased the average sinking time for the same concentration of Alkanol from 7 seconds to 5 seconds.

The effect of two entirely different types of wetting agents on each other was rather interesting. It was found that when a solution of Alkanol of a concentration which caused sinking in 10½ seconds was mixed with a soap solution which caused sinking in the same time, the mixture required 21½ seconds to cause sinking. In another experiment, the addition of 0.05 per cent of Alkanol to a 0.5 per cent solution of soap *increased* the wetting time. On the other hand, the addition of 0.05 per cent of soap to a 0.5 per cent solution of Alkanol increased the wetting power more than the addition of an equal amount of Alkanol. These results may be generalized as follows: small amounts of soap increased the wetting power of Alkanol, but small amounts of Alkanol decrease the wetting power of soap.

Affinity of Wetting Agents for Cotton

Since the molecular complexity of Alkanol is not very different from that of a simple acid dye, though it does not contain a chromophore, one would expect that Alkanol should have but very little affinity for cotton at room temperature. 35 successive determinations of sinking time were made on the same solution using a volume of 1000 cc instead of the usual 500 cc. The average sinking time at the end was 17 seconds, while at the beginning it was 21 seconds. The wetting efficiency of the solution, therefore, became slightly greater, rather than less. From this fact it can be concluded that Alkanol has no affinity for cotton and does not exhaust. This conclusion is of considerable importance in the practical use of wetting agents.

When the same experiment with regard to the tendency to exhaust was repeated for a strong soap solution, the average sinking time gradually increased from 12 seconds at the beginning of the series to 35 seconds at the end. One might think from the results with soap that soap was removed with the cotton. What happened, however, was that the solution gradually became more acid through adsorption of alkali from the soap solution by the cotton. The slight increase in acidity of the soap solution decreased its wetting efficiency.

When 35 cotton skeins were immersed successively in plain water, the water gained slightly in acidity, but much less than the soap solution, and also less than the solution of Alkanol. The latter gained in acidity less than the soap solution, however, probably because the sodium salt of a sulfonic acid is hydrolyzed much less in solution than the sodium salts of long chain carboxylic acids.

The conclusion reached from these experiments on the exhaustion of wetting agents was that cotton adsorbs alkali hydrolytically from neutral salt solutions. In the case of soap, the process will continue until all of the soap is precipitated as the free acid. In the case of salts of sulfonic acids, an equilibrium acidity is soon reached beyond which no further hydrolytic adsorption takes place. The adsorption of alkali from alkaline solutions by cotton has been reported previously by Lipatov in J. Russ. Phys. Chem. Soc. 57, 31, 48 (1927) and by Rona and Michaelis in Biochem. Zeit. 103, 19 (1921).

Conclusion

We have described for you a laboratory method for measuring the efficiency of wetting agents and have shown how that method is of value for determining the conditions under which wetting agents may be intelligently employed in the mill. It now remains to say just a word about the practical use of wetting agents by the textile industry. The chemical manufacturer can suggest various uses for wetting agents, but it remains for the mill man to demonstrate to his own satisfaction whether or not he can turn out better work at less cost if he employs them whenever a quick, uniform and thorough wetting and penetration of textile materials is essential in his processes. As an example of the ideas and prejudices which must be overcome before artificial wetting agents are properly recognized, we may cite the statement which has erroneously been accepted as a fact; namely, that cotton must be thoroughly boiled out before dyeing. We know that vat colors can be dyed on cotton which has been thoroughly wet out but not boiled to obtain excellent fastness, levelness and brightness with a considerable saving in time. I thank you. (applause.)

President Killheffer: I am sure this has been a most interesting presentation and this ingenious method seems to be a very effective one. I wonder if there is someone who would like to ask questions or make some remarks in connection with this presentation.

Mr. Harry R. Davies: Dr. Davies mentioned only cotton. Are all these conclusions to be considered equally good for woolen and worsteds?

Dr. Draves: Wetting agents are effective for wetting wool and worsteds, but wool skeins are not suitable for the evaluation of wetting agents.

Dr. Powers: Have you tried rayon skeins in your experiments?

Dr. Draves: No.

Mr. P. H. Stott: It might be interesting to know that in our laboratories we have more or less confirmed the statement made in Dr. Draves' paper regarding the efficacy of various wetting agents in relation to their concentration and also to their temperature. Working quite independently we got just about the same results that Dr. Draves has given to you.

That will just serve as a confirmation of Dr. Draves' paper. We didn't use quite the same method of testing, of course, as Dr. Draves has described, but the results I think were the same, to all practical purposes.

Mr. Ralph Wechsler: May I ask Dr. Draves if he experimented with the expelling of the air from the samples of cotton used, the effect of humidity and the condition of the cotton before making his tests, so as to be able to compare tests made one day with tests made one month later?

Dr. Draves: We find that we can reproduce results remarkably well. That is, with the average humidity in the laboratory we can get about the same results six months later with different batches of yarn and with different conditions of humidity in the laboratory.

Mr. Wechsler: I ask that because some time ago we did some work with silk. We attempted to measure something by the time of sinking and got very discordant results until we found that the drying out of the skein and then permitting it to reabsorb natural moisture or drying it in the dessicator affected those sinking tests considerably. Of course, in the case of silk there is the gum to consider which is an added factor that you don't have present in cotton.

Dr. Draves: Very probably slightly better results might be obtained in the evaluation of wetting agents if cotton skeins were employed which have been conditioned at a standard temperature and relative humidity. However, preliminary experiments seemed to show that differences in average sinking time were small for a given concentration of wetting agent between skeins dried over calcium chloride, skeins conditioned at a relative humidity of 66 per cent over a saturated solution of sodium nitrite and skeins left in the air of the laboratory. Since the conditioning of so many skeins would have involved considerable bother and since we could obtain reproducible results with skeins directly out of stock, we have not taken the trouble to use conditioned skeins.

I might say, however, that in testing the wetting properties of absorbent paper, we have found that it is very important indeed to condition the paper.

Dr. Jos. F. X. Harold: I should like to ask if there is any relation between the maximum detergency of soap and the maximum wetting power.

Dr. Draves: The detergent power of soap, if I am not mistaken, is supposed to be due largely to its ability to peptize particles of dirt and to emulsify fats and oils. I am not sure that explanations for the exact mechanism of these peptizing and emulsifying actions are generally agreed upon, but the ability to lower interfacial tension is undoubtedly involved. The adhesive power of the particle of dirt for the fabric is also said to be lowered by the preferential adsorption of soap. I am sure that there is something more than just lowering of surface tension, that is wetting power, involved in detergent action, however, because there is no better wetting agent than alcohol and yet alcohol is certainly not a detergent, although alcohol does have solvent properties.

Dr. Killheffer: Thank you very much.

FEBRUARY MEETING OF NEW YORK SECTION

THE February meeting of the New York Section of the American Association of Textile Chemists and Colorists convened Friday evening, February 27, 1931, at 8:15 o'clock, at the Building Trades Employers' Association, 2 Park Avenue, New York City, Mr. Robert H. Gaede, Chairman, presiding.

The regular business of the Section was transacted.

Chairman Gaede: If there is no further business to come before the meeting we will go on to our first paper, "The Importance of Adsorption and Other Colloidal Phenomena in Plant Operations," by Mr. Pierce M. Travis, who is a consultant, principally along colloidal lines, colloidal chemistry, and who has spoken before the Association previously.

Mr. Travis! (Applause)

Mr. Pierce M. Travis: Mr. Chairman, Members of the Association: I am very glad to be here this evening to address you briefly in regard to the principles of colloidal chemistry. As you all know, it is a fairly young science but is coming forward more each month. Since the time of Graham, who was the father of colloidal chemistry, it has made very rapid progress and colloidal principles are being viewed with more importance almost daily, and a great many of our problems of today really involve the principles, the basic principles of colloid chemistry. So I thought it wise to briefly review some

of the elementary principles that apply generally in the case of colloidal problems and also to lead into some of the basic fundamental principles of adsorption, which is becoming more important daily in the colloid field. You gentlemen who are interested in dyestuffs know the importance of the principles of adsorption.

Mr. Travis presented his prepared paper. (Applause)

The Importance of Adsorption and Other Colloidal Phenomena in Plant Operations

By PIERCE M. TRAVIS

RESEARCHES with the ultramicroscope have shown that we can divide dissolved substances into three groups, depending on the state of subdivision: (1) particles that can be observed under the microscope are called microns; (2) particles that can be observed only by means of the ultramicroscope are called ultramicrons or submicrons; and (3) particles that remain invisible in the latter instrument are termed amicrons. The boundaries between these three groups cannot be sharply defined, since the visibility of a particle does not always depend on size. As a first approximation, we may say, however, that the limit of microscopic visibility lies at 0.2μ, while the limit of ultramicroscopic visibility lies around 10 Mu (1 mm = 1000 μ; 1μ = 1000 Mu; 1 Mu = 10 AU Angstrom units).

It may be said that in true solutions matter is split up into molecules or ions while in colloidal solutions, larger particles, polymolecular particles, are present.

It is customary to call a colloidal solution a SOL, while the name GEL is used exclusively for the jelly-like mass formed, when, for instance, a gelatin solution solidifies completely without any visible separation.

When light strikes a colloidal solution, it is partly reflected and partly transmitted, the liquid presents a turbid appearance or Tyndall effect.

If gum mastic is dissolved in alcohol, a true solution is obtained. On pouring a little of this solution into water, we obtain a colloidal solution of mastic in water, as shown by the immediate appearance of the TYNDALL effect. We speak of INTERNAL and EXTERNAL PHASE and call the dispersed particles MICELLES or GRANULES.

Graham, who was the father of colloid chemistry, was mistaken in his classification of colloidal and non-colloidal (or crystalloidal as he called them) substances, since, in general, any substance can be brought into the colloidal state. Colloidality is not a specific property of a definite type of substances; but represents a possible state, comparable with the liquid state, the gaseous state and the solid state. In other words, it is the colloidal state of matter.

Moreover crystallinity does not stand out in striking contrast to colloidality for X-ray researches have shown that in the large majority of colloidal systems the dispersed particles are minute crystals.

One of the most important properties of colloidal particles is the fact that they are generally electrically charged with respect to their surroundings. When an electric current is passed through a colloidal solution of As_2S_3, it will be found after a while that the dispersed substances have accumulated at the anode. Without claiming that anything else has occurred in the liquid but the displacement of the As_2S_3, one may state that the sulphide has migrated as a whole, whereas in a solution of electrolyte, sodium chloride, the chlorine moves toward the anode and the sodium toward the cathode as ions.

Furthermore, the direction in which a colloidal particle moves, with respect to the electric current is a specific property of that particle. As_2S_3 particles move toward the anode and are, therefore, apparently negatively charged, while particles of Fe_2O_3 move toward the cathode and are, therefore, positively charged. A sol of ferric oxide may be prepared by hydrolyzing ferric chloride at higher temperatures. On pouring a few drops of a solution of this substance into boiling water, hydrolysis takes place and a reddish-brown iron oxide sol is formed. If this solution be placed in a dialyzer, the hydrochloric acid which is formed passes through the parchment into the outside water phase.

It has been known for some time that colloidal solutions are extremely sensitive to small quantities of added electrolytes.

For a negatively charged colloid, the amount of electrolyte required to produce precipitation is determined by the valences of the cation, the valence of the anion being of subordinate importance. For a positively charged sol, the valence of the anion determines the precipitating power of an electrolyte.

Therefore, a monovalent ion has a mild flocculating power; a divalent ion has more; while a trivalent ion is still more powerful; and so on. In the case of the As_2S_3 sol, the coagulating point (or limiting value) i.e. the concentration of the electrolyte required to precipitate the sol completely is 56 millimoles per liter for KCl, 0.68 millimoles per liter for $BaCl_2$ and 0.091 millimoles per liter for $AlCl_3$. Hence the flocculating powers of these electrolytes are in the ratio of 1:8:500. The converse of these relationships is presented by the previously mentioned positively charged Fe_2O_3 sol. Whereas, 60 millimoles of KCl (monovalent anion) were required for precipitation, only 0.6 millimoles of

K_2SO_4 (divalent anion) produced the same effect in reaching the iso-electric point.

Colloidal systems have three general characteristics: (1) they are not optically void but show the TYNDALL effect; (2) when dialyzed they appear to contain particles that do not pass through parchment; and (3) they migrate under the influence of a difference in electric potential. Although colloidal systems have all these properties in common, they fall, nevertheless, into two large classes. The two groups have been designated as SUSPENSOIDS and EMULSOIDS. In another classification the terms LYOPHOBE and LYOPHILE are employed.

(a) The suspensoids or lyophobe colloids to which belong the metal sols, the hydroxide sols, and the sols of inorganic salts, are systems which in most of their physical properties differ only slightly from their dispersion media. The viscosity of a gold sol or an arsenic sulphide sol differ little from that of water. Emulsoids or lyophile colloids, which include the sols of albumin, casein, gelatin, etc., form disperse systems in which the properties of the dispersing phase are considerably modified by the dispersed colloid. The high viscosity of a glue solution is a familiar example.

(b) There is an important difference in the behavior toward electrolytes. Suspensoids undergo flocculation by the addition of minute concentrations of electrolytes, whereas large amounts of an electrolyte are necessary to precipitate emulsoids; i.e., the salting out of proteins requires comparatively large concentrations of electrolyte (except in the case of salts of heavy metals). There is also another important difference in the precipitation of these two groups. Addition of water to the system after flocculation causes emulsoids to return to the state of colloidal dispersion, but does not have this effect upon suspensoids; hence flocculation, as a rule, is irreversible, for suspensoids, and reversible for emulsoids; that is, the suspensoids became denatured.

(c) The ultramicroscopic image of one group is often different from that of the others. Most suspensoids give a well-differentiated ultramicroscopic picture consisting of bright particles in vigorous Brownian movement. Emulsoids, however, usually show only a diffuse light cone or Tyndall effect.

(d) Finally, the electrical properties are quite different. A suspensoid ordinarily, has an electric charge of a definite sign, and only by special methods is it possible to change this sign. On the contrary, most emulsoids, more particularly protein sols, change their charge readily, so they are positively charged in an acid medium and negatively charged in an alkaline medium as on changing of the pH value.

It follows that there is apparently not a mutual relation between the suspensoid particles and the dispersion medium. Hence, the properties of the latter hardly change, whereas in emulsoid systems, which are rightly called lyophile or water loving, a reciprocal action between the dispersed phase and its medium takes place.

It has been shown that colloidal systems are systems in which a substance, although not in true solution, is present in a state of fine division. The question arises: How is it possible for such a system to maintain itself? As we know, the boundary between each particle and the dispersion medium is the seat of an interfacial energy which always strives to unite the particles in order to reduce the interfacial area. This tendency of particles to unite and form larger aggregates is well known: small droplets tend to unite and form drops: small crystals grow together and form larger units.

Since the particles in a colloidal solution are in Brownian movement, they are continually in a condition to collide with each other. At first thought, it is inconceivable why the boundary tension just referred to does not cause the particles to cling together whenever a collision occurs, and thus destroy the colloidal system. It is an equally striking fact, that, at least in the case of suspensoids, the addition of a small quantity of electrolyte brings about a condition which really is in agreement with this expectation: on the addition of an electrolyte the dispersed particles unite, the system exhibits flocculation, and the disperse system is destroyed when the charge is neutralized.

Secondly, the large part played by electrolytes in connection with the fact that most sols are electrically charged, gives rise to the assumption that special electrical charges have an important bearing on the situation. This requires consideration of surface tension and boundary phenomena or adsorption.

The best-known boundary phenomenon is that which exists at the surface of a liquid in contact with saturated vapor or air. We are all familiar with the appearance of a concave or convex meniscus with the rise and fall of liquids in capillary tubes.

This is due to the action of surface tension, which exists at the surface of all liquids and is a force acting parallel to the boundary surface tending to decrease the surface to a minimum.

Hence, an increase in surface requires expenditure of energy, since it is a movement against the direction of the force. The surface is, therefore, the seat of a surface energy; so, if we define the surface tension as the force that operates in each square centimeter of cross-section of the surface to hold it together, the surface energy must be the work necessary to increase the surface by one square centimeter (at constant temperature).

As an example of the effect of surface tension, it may be noted that small droplets tend to distill to larger ones. This can readily be observed under the microscope by placing a number of drops in the cell of a microscopic slide. It is evident that small drops have a greater vapor pressure than large ones, since one gram of small drops has more potential energy than one gram of large drops.

If both are to be vaporized, different amounts of energy will be required; hence the two kinds of drops cannot exist in equilibrium with the same vapor. Similarly, since small crystals sublime to large ones, we may conclude that there also exists a surface tension at the boundary of a solid in contact with its vapor.

It follows that the amount of compression resulting from surface tension becomes greater as the radius of the particle becomes smaller. It is, therefore, possible for the density of small particles to be greater than the density of the larger aggregates from which they were derived. This condition will adjust itself at the first opportunity. Everyone is familiar with the way mercury droplets will coalesce into larger drops when rolled round on the surface of a dish.

Only mercury, molten metals and fused salts have surface tensions which exceed that of water.

Organic substances, particularly those that have a long chain of carbon atoms or one or more benzene rings, exert the greatest surface activity, that is, cause the greatest change in the surface tension of water. In general, the surface activity as an homologous series increases with the number of carbon atoms.

The speed with which a dissolved substance changes the surface tension of water is generally great. Within a few seconds, the surface tension reaches its final value. Since the process does not, however, take place instantaneously we must distinguish between a dynamic and a static surface tension. The former is measured at a newly formed surface, whereas the second belongs to a surface that is completely in equilibrium with the interior of the liquid. Once in a while it happens, as for instance in the case of soap solutions, that the time required to establish equilibrium is quite considerable.

Another important property, common to systems of more than one component, and known for a long time, is that the concentration in the interior of the liquid and that in the boundary layer are not always the same. In the boundary layer, the concentration of one of the components is often much greater than in the liquid itself; sometimes, however, it is smaller.

If a substance lowers the surface tension, the boundary layer is richer in this substance than the bulk of the liquid, and, conversely, if the substance raises the surface tension, the boundary layer is poorer.

Variations in the concentration in the boundary layer are commonly called adsorption. Positive adsorption is that which occurs when there is an increase in concentration; if a decrease in concentration in the boundary layer takes place, the adsorption is said to be negative.

Positive adsorption is a much more important phenomenon than negative adsorption. This becomes clear if we consider only the two cases. Suppose we have a liquid of a certain concentration. Then the increase in the concentration of the boundary layer is, so to say, unlimited; hence a very dilute solution can be extremely concentrated in the boundary layer. If, however, negative adsorption takes place, the concentration of the boundary layer can, in an extreme case, be equal to 0, but the boundary layer can never contain less dissolved matter than is present in pure water. While, for positive adsorption, the concentration can increase without limit, it can decrease only to a certain extent in the case of negative adsorption. Accordingly, we see that positive adsorption plays a more important role than negative and is more pronounced for very small concentrations.

At the boundary between two immiscible liquids, there also exists an interfacial tension. This is evident at once from the fact that a small amount of oil introduced into water forms a round drop (flattened only by the force of gravity). We conclude that there is a tendency toward minimum surface; consequently, surface energy is present at the oil-water boundary.

It is generally known that gases condense at the surface of adsorbents or, in other words, that gaseous adsorption takes place at the solid-gas boundary. A piece of charcoal, previously heated over a flame, on coming in contact with ammonia gas collected over mercury in a eudiometer tube, causes an immediate rise of the mercury column, due to the condensation of gas at the surface of the charcoal.

In the first place, we notice that adsorption is reduced to a process of chemical affinity, and yet it is not specific in character, being thus in striking contrast with the specific nature of chemical combination. The supporting evidence includes the fact that the chemically inert gases, helium and neon, are scarcely adsorbed by charcoal. It should be remembered, however, that argon is truly absorbed.

Secondly, the theory is based on the idea that the adsorbed layer is only one molecule deep; otherwise a covered space would also be able to adsorb. Although the hypothesis holds true in certain cases, it is, as a general statement, open to grave doubt.

The phenomena of gaseous adsorption show very clearly that the adsorption equilibrium is a reversible one. For instance, if we increase the volume after

the adsorption equilibrium has been established, the carbon releases as much gas as is required, in accordance with the change in pressure due to the increased volume.

A large surface, such as occurs in the case of amorphous carbon, cannot in itself be considered a sufficient reason for a great amount of adsorption; we frequently meet with large surfaces that adsorb only slightly. This is easily understood in view of the facts mentioned above. The adsorption process is determined not only by the surface capacity but also by the influence of the substance to be adsorbed on the boundary tension. This naturally varies for different substances.

One of these is the manner in which a mixture of two gases are adsorbed. It may be stated here that in most cases both gases are adsorbed from a mixture of the two, but each is adsorbed to a lesser extent than if it were present alone. A certain mutual displacement exists, therefore, but in spite of this the completely reversible character of adsorption phenomena is maintained, the final equilibrium being independent of the order in which the gases are brought in contact with the adsorbent.

The speed with which equilibrium is established in this case is quite considerable. A few minutes are more than sufficient to bring about a perfect adsorption equilibrium. If, however, any chemical reaction takes place subsequently, either between the gases and the adsorbent, or between the gases themselves in the adsorption layer, more time will be required to reach a final state of equilibrium.

If a number of small crystals are in contact with their solution while at the same time a few larger crystals are present, it is quite apparent that the smaller crystals are more soluble than the larger ones; hence the former dissolve continuously and the latter grow, since the solution is supersaturated with respect to the larger crystals. This phenomenon must likewise be explained on the supposition that a boundary energy plays a role just as with small drops which have a greater vapor pressure than larger ones. This interfacial tension is as yet not accessible to measurement.

It has been known for a long time that the constituents of a solution can be removed by means of charcoal powder or other adsorbents. Colored substances, in particular, are often removed in this manner. When an adsorbent is added to a solution of a dye, the intensity of the color will decrease or the color will disappear completely, depending on the amount of adsorbent used. The same thing happens when a quantity of wool is employed. The adsorption of the color becomes manifest by the dyeing of the adsorbent.

Such are catalytic phenomena, enzyme reactions, and the effects of disinfectants and poisons. In all these cases, where extremely small concentrations have great effect, this action is due to the fact that somewhere an adsorption plays a role and a minute concentration is considerably increased in some boundary layer. It is perhaps not a mere coincidence that most of these substances are characterized by great surface activity, but adsorption processes are characterized by a rapid attainment of the final state of equilibrium.

While it is true that a large surface is not sufficient to produce a high degree of adsorption, it so happens that substances that have great surface activity under one set of conditions are also well absorbed under others. For an homologous series this regularity holds quite well; but phenol lowers the surface tension of water less than amyl alcohol, yet, the former is, nevertheless, better adsorbed.

The adsorption is slight for all inorganic substances with the exception of the halogens. Moreover, the salts of the heavy metals are adsorbed to a somewhat greater extent than those of the alkali metals. This is also true of all aliphatic substances having several hydroxyl groups, such as the sugars.

The adsorption is strongest, generally speaking, for aromatic substances. The more benzene nuclei they contain, or the more complicated their structures are (as in the case of the dyestuffs,) the better they are adsorbed.

It may be stated in a general way that, apart from constitutive differences, a more complicated molecular structure coincides with greater adsorbability.

The equality of the order of adsorption in various adsorbents is of considerable importance because in colloid-chemical discussions we often deal with adsorption processes that cannot be measured directly for colloidal particles .The corresponding adsorption experiments have usually been carried out by means of a suitable charcoal powder or silica gel; hence, it is worth knowing that the order of these phenomena is the same in different adsorbents, and that some of the results may be transferred from one series to another.

The influence of the temperature on the adsorption process is generally small. Ordinarily, adsorption decreases with rising temperature.

Sometimes we meet with cases in which higher temperatures are conducive to the adsorption process. In general, boundary tensions decrease with rising temperature; the liquid-gas boundary tension, as is well known, approaches zero; when the critical temperature is reached and the boundary or surface tension becomes zero.

The influence of the medium on the adsorption process may be embodied in the following rule: a substance that is easily adsorbed is a poor adsorption medium. For example, alcohol dissolved in water is fairly well adsorbed by carbon. A dye that is well adsorbed from its aqueous solution is poorly adsorbed from an alcoholic solution. Since alcohol itself is so well adsorbed, it is a poor adsorption medium.

The above statements indicate clearly that we can often successfully remove a substance, adsorbed in an aqueous solution, from the adsorbent, by pouring over it a liquid that is well adsorbed itself and hence is a poor adsorbing agent. This may possibly be connected with the fact that phenol dissolved in water is a strong disinfectant, while its action as such is far less when dissolved in oil or in alcohol. At any rate, this fact corroborates the statement that adsorption processes probably play an important role in disinfectants.

In adsorption phenomena the question frequently asked is: Does the adsorption go on indefinitely with increasing concentration, or do we finally reach a state of saturation? In fact, there are indications that in some cases the adsorption isotherm runs horizontally at higher concentrations. Even so, the impression prevails that Langmuir's and Harkins idea of a monomolecular layer covering a surface is not always true.

Our insight into the condition of some substances in the adsorbed state, especially of those that are polar, has been considerably extended by the work of these investigators, who arrived, by different methods, and independently of each other, at the same conclusion, briefly formulated as follows: At an interface the molecules do not lie at random, but are oriented in a definite manner.

Furthermore, the reason why polar organic compounds accumulate, that is, are strongly adsorbed, in boundary layers, now becomes apparent. Let us consider, for example, a layer of benzene placed on water. On adding butyric acid to the system, we notice that this substance dissolves to a large extent in the benzene (organic substances generally are quite soluble in organic solvents), but only slightly in water, in spite of the fact that its COOH group is attracted to the water. Consequently, however small the concentration of the acid may be in the benzene layer, the butyric acid molecules move preferably toward the boundary layer where part of the molecule, viz., the carboxyl group, can remain in the water, and the rest, i. e., the hydocarbon chain, in the organic solvent. The result is, therefore, accumulation of the butyric acid in the interface, in other words, strong adsorption.

The adsorption layer thus becomes a typical transition layer; the two media are separated by an intermediate layer which consists of a hydrocarbon radical on one side and a carboxyl group on the other. As a confirmation of the adage—like dissolves like—each part of the molecule dissolves in the medium that is like it.

These conclusions may be very helpful in the elucidation of several colloid-chemical phenomena; for example, the phenomenon of adsorption is most important in stabilizing an emulsion as a suspensoid.

The necessity of having traces of an electrolyte for stabilizing a sol has been known for a long time also. Stabilizing a colloid by the addition of a substance is called peptization. It should be clear in this connection that a stable colloid always contains traces of electrolyte. Usually these traces are present in the preparation of the sol. If one should try to remove them purposely by excessive dialyzing, then it can only be done at the expense of the stability. Graham found, for instance, that excessive dialysis of ferric oxide causes the sol to flocculate in the dialyzer.

No one can be blind to the fact that current theories are far from adequate. The more the investigations considered are extended and applied, the more one realizes that the picture drawn has been highly idealized. With an extension of the theory presented, possibly a radical improvement may be expected. It is wise, therefore, to consider theory merely as a link in the long chain of interpretations of scientific facts.

Chairman Gaede: I would like to ask if there are any questions which anyone would care to ask Mr. Travis on this paper?

Mr. Sidney Springer: Will electrolytes stabilize colloidal solutions of dispersoids?

Mr. Travis: In the case of dispersoids, the electrolyte will stabilize it if it is of the right charge. Of course, if you have an opposite charge, you will neutralize and you will get flocculation. But, in the case of dispersoids, the electrolyte is the important factor of stabilization.

Mr. Fred Bauman: Did you say, Doctor, that the larger the molecule, the quicker it will be adsorbed or the more of it will be adsorbed in a certain series?

Mr. Travis: If the molecule contains a series of benzine radicals, or something of that sort, the more complicated the molecule, as a general rule, the more readily is it adsorbed. That is of course not a positive rule, but it is so, generally speaking.

Take some very complicated organic compounds and you can usually remove them by some adsorbent more readily than the simple elementary combinations like methane or ethane.

Mr. Bauman: Isn't it true that the bigger the molecule, the more insoluble it becomes, and therefore the harder it is to adsorb?

Mr. Travis: Not necessarily, if you have the proper adsorbent agents. Take as an example silica gel, which is one of the popular ones today. Some of the largest, most complicated molecules have been adsorbed successfully with the use of silica gel.

Of course, it depends upon the nature of the adsorbent. There is no rule in adsorption that is positive. You probably realize that in the working of adsorption principles it has been more or less hit-or-miss and that the theories are just being more or less correlated and that we have just the sign-posts here, and there. We haven't reached the ultimate solution in adsorption.

I had a problem in the laboratory about two months ago where I expected a high degree of adsorption. The client was mixing two substances together to obtain his adsorption and I found in the case of one that he was using he was just simply wasting the material. It was nothing but the glycerin that did the adsorption on cloth and that was where he was getting his high degree of adsorption. I didn't expect glycerin to be the adsorbent, but it proved to be. This was in a case where they were using triethanolamine combinations.

But as a general rule, the more complicated the molecule, the more readily you can work with it, with the modern adsorption agents such as charcoal, silicate gel, glycerin, and such things. That is not an infallible rule, understand. It applies, say, just in ninety per cent of the cases. It doesn't always work out that way.

Mr. Bearse: You speak of an electrolyte having a proper charge, in addition to colloid suspension. My concept is that the electrolytes ionize and their charges are balanced.

Mr. Travis: No. Take, for instance, a case where you have ferric oxide, which takes a positive charge. Then, if you add barium chloride, for instance, where there are two positive charges on your barium, and there will be more or less of a peptizing action. While the chlorine of course has a negative charge, the one that predominates is the metal that has the positive charges in that case, two positive charges.

If you took the reverse condition, i. e., potassium sulphate, where you had K_2SO_4, where the sulphate radical had the two negative charges there would be a tendency to flocculate. The other part of the electrolyte does not have much action.

That is a peculiar thing in the stabilizing problem; that you take the one with the greatest charge of the nature of the dispersoid, and the way we determine which charge the dispersoid has is usually by the common electrolytic method, taking a U tube and passing a current through and seeing which way it migrates, to the anode or cathode, then picking out the traces of electrolytes of like charge, for stabilization.

Of course, there is another principle involved there. If you are using a gelatin or an emulsoid and adsorbing it on the surface of the suspensoid, for protection, then you encounter other conditions. I have made suspensoids which would stand both negative and positive charges without affecting them, but it was due to the coating of the emulsoid on the outside, which I was getting my stability from, and not from the suspensoid itself.

Take the case of a gold sol. In order to make it stable you have to add a trace of an electrolyte. Otherwise it will flocculate.

But those electrolytes that are added of course are added in small quantities. Usually, the stability is figured on, allowing about twenty to thirty millivolts on the charge.

Mr. Springer: How about the case of diatomic molecules such as soidum chloride or calcium sulphate?

Mr. Travis: In the case of sodium chloride you have your monovalents, the di in the potassium sulphate.

Mr. Springer: They each carry one charge, don't they?

Mr. Travis: The sodium chloride and potassium sulphate, did you say?

Mr. Springer: Sodium chloride or calcium sulphate.

Mr. Travis: In the case of the calcium sulphate, the two positive calcium charges would predominate and would have a tendency to flocculate a negatively charged dispersoid, while if it was positively charged it would encourage the suspension up to a certain limit. These quantities I am speaking of are small amounts, of course. If you finally go up to a very high concentration then it does not apply. The other portion of the electrolyte becomes a factor, but in small amounts, say, around sixty milligrams per liter, or something like that—small amounts of concentration. That is where the stability factor comes in, in just minute quantities.

Mr. Springer: Didn't you state a definite rule then that if the negative radical and the positive radical carry the same number of charges, the positive radical will predominate?

Mr. Travis: In the case of sodium chloride, or monovalent, it takes a great amount of electrolyte to cause a precipitation for the reason that you have a monovalent metal present.

If you increase that to barium chloride, instead of taking, say, sixty milligrams per liter, it will take about six-tenths of a milligram per liter. The ratio comes down enormously. The same thing is true if you again increase it to an aluminum chloride, where you have three charges on the aluminum radical. Then it comes down to about one to five hundred. In other words, the precipitating values are not in direct relation like in chemical valences but the charges come down in enormous ratio as you increase the metallic part of the salt if the suspensoid has the opposite charge.

Mr. Springer: I see that, but in that case aluminum

chloride would show a negative reaction toward the suspensoid.

Mr. Travis: Your aluminum with the three positive charges would show an extreme positive reaction, and if you add a suspensoid with a negative charge, such as AS_2S_3, which is negatively charged in suspension, you will get an immediate precipitation.

Mr. Springer: But what I want to know is, in the case of calcium sulphate, where they both carry the same valence—you have, say, one atom of calcium, or take the case of potassium chloride, where you have one atom of potassium and one of chlorine—how are you to know which charge is predominant?

Mr. Travis: By adding. If you take a small amount of sodium chloride and do not get a flocculation and then add a small amount of potassium sulphate and you do get a flocculation, you know right away that your suspensoid has a positive charge, without using the electrical method.

Mr. Walter C. Durfee: I had an idea from hearing these things and thinking about them that aside from the positive and negative charges and all that, the phenomena was caused a great deal by a regular cohesion. That is to say, we have a particle here and we put something in the water and sometimes it precipitates it and sometimes it peptizes it. But apparently the clue to the thing is that it is a cohesion between this particle and something else and if the thing that sticks to it happens to be positive it may increase the peptization. If it happens to be negative, it may precipitate it.

How does that work out?

Mr. Travis: Probably I can clear that up in another way. I haven't made that clear apparently.

In the case of putting the charges on the particles of the suspensoids, the poly-molecular groups, if they are negatively charged, and we add, we will say, potassium sulphate, so as to encourage the sulphate radical with the two negative charges in suspension, that will increase the charge on the dispersed particles, and therefore when they come near together, like charges repel, and having like charge, they repel from each other and are kept in suspension in that way.

It is the same way with negative charges. If they are negatively charged or positively charged, like charges repel, and in Brownian motion, where you have the particles very finely divided, you know that on examining under the microscope or ultra-microscope, you can see these particles constantly bombarding through the mass, which is due to the molecular bombardment. The particles are so small that the particles of water which are constantly in motion keep kicking it around like a football and you get Brownian motion, which Robert Brown when he first discovered it thought he had discovered the cells of life. However, it is nothing at all but the molecular movement of the particles. Brownian motion begins to appear when you get down to particles of about three microns. You commence to notice it then and as you decrease below that it becomes more active because of molecular bombardment, and when you get down to particles of two-tenths of a micron, which is about the limit of the microscope, you have very active Brownian movement. And of course if the particles all have a like charge they are repelled. But if you add an electrolyte with an opposite charge, which removes that charge from all these particles then they do flocculate and down they come.

That is a modern theory of what causes the flocculation.

Very often, you know, in precipitation, they will take such things as alum to flocculate. Alum is a very good bet because a great number of the dispersions are negatively charged and when you add the alum with the three charges of the aluminum you neutralize those charges. They can no longer repel each other and they collide, and when they do that they flocculate. In other words, they coalesce and down they came. When the particle grows in size, gravity acts and out it comes from the solution, while in the case of Brownian movement they are suspended and remain suspended because of the Brownian motion. They do not settle because gravity is no longer to be considered. You have a world in itself. The Brownian motion keeps them all in suspension and they will remain that way for years, provided they do not release that charge, which is normally there on proper dispersion.

Mr. Bonnar: I should like to hear you tell a little more about the triethanolamine and glycerin combination you spoke of a minute ago.

Mr. Travis: I would like to tell you something about that but it was in connection with some patent work which was just filed in the Patent Office about two months ago for one of my clients and I don't think he would thank me if I went into a description of it here this evening. (Laughter)

Chairman Gaede: That is a very good reason.

Mr. Henry F. Herrmann: Mr. Travis, I don't know whether I understood that phenomena correctly when you spoke of butyric acid dissolved in a layer of benzene floating on water disassociating. Would it be possible to pour the benzene off of there, have it separate from the identity of the acid?

Mr. Travis: What you get is a boundary layer due to adsorption. That is one of the famous experiments of Langmuir which was afterwards followed by Harkins, who has done a great amount of work in connection with adsorption, and was one of the first proofs presented which was more or less positive that the molecules when they form about a particle, or the adsorptive layer at the interface between two immiscible surfaces, are oriented and that the carboxyl group goes toward the water phase,

if water is the outer phase, and the hydrocarbon goes toward the organic solvent, which it naturally wants to dissolve in, but the carboxyl group is pulled by the water so that it goes in the interface. There is an attraction of the water on the carboxyl group and the hydrocarbon or other carbon groups, are attracted toward the organic, so they orient around the particles and form this shell or protection envelope, which is the principle that we use in emulsification, when we add soaps, etc., as emulsifying agents.

Mr. Herrmann: They do not become detached from one another?

Mr. Travis: No, they are supposed to be oriented and are supposed to be one molecule thick, but that is not always true. They evidently form wedges and some of them wedge in between because I have had cases in the last few months in investigations I have been making, where I was adsorbing on the surface of the particles, to keep them from coalescing, in making proper adhesives, and have them set at the proper time and form protection coatings. I figured back to the quantity required, one molecule thick, and I found that that was my limit all right. But I also found by centrifuging out that I could go up beyond that limit where there was a molecular coating and still I couldn't throw the other out of the interface.

So there must be an additional attraction although the theory of Langmuir and Harkins is that we form a shell, or polar groups, as they call them, with the carboxyls facing out and the hydrocarbons in, to form the molecules around the sphere, which of course is the principle of adsorption. And that is a typical demonstration of it, taking the butyric acid and dissolving it in the organic solvent and then adding the water, and it will immediately go down into the boundary surface, due to this attraction of the carboxyl group for the water, and you can remove it. Yes, you could remove it from the solvent, provided you decanted the other solvent.

Mr. Herrmann: You could just decant it and remove all of the butyric acid?

Mr. Travis: No, the solvent which would be on the surface and the butyric acid would be at the interface, and you could adsorb it or remove it from the organic liquid.

It is the same thing with certain dyes, as you probably know, in water phase you can add alcohol and get them out, that is, from an adsorbent. It is a matter then of which one it has the greatest affinity for. It is a common practice. Principles of adsorption have been practiced for years in ordinary chemical operations, such as in precipitating certain groups. You know that you add other reagents to remove impurities. That is nothing but a question of adsorption. The other material we add has a greater adsorbent value than the traces of material which are left and we purify our salts in that way.

That has been a practice for years, and the principle of adsorption comes in there of removing by mechanical means, surface attraction, and this matter of adsorption is really not a valency. In other words, you can have a thing saturated as regards valency and still adsorb. There seems to be an additional affinity there which everyone who is working in adsorption wants to get the answer for, but we can't explain it as yet. There has not been any proof to substantiate what takes place there.

We know there is an attraction there similar to a bond attraction but not quite as strong that pulls the material out.

Chairman Gaede: Are there any further questions?

Mr. Springer: Can it definitely be stated that if two suspensoids are mixed, for example, a gum in water and a dyestuff in water, one will tend to stabilize the other providing they both carry the same charges?

Mr. Travis: Of course, in that case you are mentioning an emulsoid, your gum, if it is soluble in water—

Mr. Springer: I meant to say emulsoids.

Mr. Travis: In the case of an emulsoid, if you have an emulsoid which will coat around the particles, then of course you get a condition in which you can add an electrolyte and still not flocculate it because of the emulsoid protection. If you can get the emulsoid to be adsorbed on the surface of the suspensoid, then you can depend upon the stability of the emulsoid to hold it up.

As a matter of fact, that is common practice. Let us say we have a vat dye and we want to hold it in suspension. Well, we add a little gum tragacanth and a little acacia to it and a little gelatin, a few things like that, and finally we get a condition which enables us to retain it in suspension.

We are using the principle there of the emulsoid forming a film or protection or envelope about the particle. So it is the emulsoid then that is holding it in suspension rather than electrical charge.

The suspensions I mentioned we classify in two groups, suspensoids and emulsoids. A straight suspensoid is one in which you have no emulsoid present, such as gelatin, and you have to depend upon electrical charge for your stability and that electrical charge must be in small quantities and must be of the same nature as the type of charge which the suspensoid takes when it is put into water, and all matter dispersed in water takes one charge or the other, negative or positive, depending upon the nature of the material.

Chairman Gaede: I don't like to interrupt this interesting discussion but we have another paper to present and if we have any time later and there are further questions we may take them up at that time. This paper and discussion certainly has cleared up some questions that

we have had in our minds regarding adsorption and has opened up new ideas.

The next paper is by Dr. E. W. Pierce, of the Ciba Company. Dr. Pierce has had a number of years' experience in the practical end, and a great deal of experience in the laboratory. His paper is on "Practical Dyeing and Printing as Influenced by Colloid Chemistry."

Dr. Pierce! (Applause)

Dr. Pierce presented his prepared paper. (Applause)

Practical Dyeing and Printing as Influenced by Colloid Chemistry

By Dr. E. W. Pierce

Ciba Co.

IN FORMER years all the phenomena and problems of the dyehouse and print shop were explained by the rules and reactions of chemistry as it was understood at that time. But there were, and still are, many things that will not stay explained, if we simply put down the reaction on paper and try to follow what has happened; there is some unruly spirit that enters into our calculations and, to use a current slang phrase, gums up the works. Gums up the work, was a fortunate selection for a descriptive phrase since gum and gum-like substances were the first colloids to be studied and since then we have seen that most of our dyes and dyeing operations have a nature closely akin to the gums themselves. As I cannot foresee that the other speaker of the evening will or will not give a definition of colloids or will assume that you are already familiar with this interesting state of matter, I am forced to define my terms. You are all familiar with a true solution, such as you form when salt is dissolved in water, but are you really sure you have a true solution in other cases? Let us take Bichromate of Soda, because it has a high color and can easily be seen; a solution of Bichromate spotted on a piece of filter paper will give a spot that spreads, so will a solution of Acid Orange and so will a dilution of a vat dye orange. Let us compare the spots produced by these three liquids; the Bichromate will have spread as far as the amount of liquid permits and there will be a full color uniform to the outer limits, the Acid Orange will show color almost to the limits but there will always be a ring of pure water around the color spot while the vat dye will have but a small color spot and a much larger area of pure water around it. The back of the paper will also vary in the depth of color that shows on it. In a true solution the dissolved material only parts with its water by the old established laws of chemistry, but in the other cases the bond is a looser one and conditions other than chemical reactions are able to effect the separation. Let us add common salt to the dye solution and note that after a time the liquid has become clear and the coloring matter has settled as a precipitate at the bottom of the container; no chemical change has taken place for the salty water may be poured off and the dye put into solution again with more fresh water, in fact this very principle is made use of in the manufacture of most of the ordinary dyestuffs. The explanation of the colloid state of matter is that the particles or molecules are not dissociated or ionized when dissolved in water and remain in small groups or masses that are in suspension or dispersion, but do not have that freedom of motion which is characteristic of a true solution. If the groups or masses grow in size, for any reason, then they lose their state of dispersion, no longer remain in suspension and fall as a precipitate. Heating, freezing, addition of soluble salts or the presence of another colloid of opposite electric charge will bring about this precipitation and, in return, the presence of a colloid will generally prevent a normal chemical reaction from proceeding in a normal manner. It is well to note that the lines of division between true solution, colloid and well dispersed precipitate are not sharply drawn and one class may merge in the other; to illustrate, we may have a dyestuff that is capable of crystallization and seems to form a true solution, but which is still a colloid and we may have mechanical dispersions that partake of all the character of natural colloids.

I mentioned how the dyestuffs in solution are thrown out by the addition of salt so they may be filtered, dried, ground and sold to the user in powder form. Colors like Methyl Violet or Rhodamine where the presence of salt might lessen the solubility, may be frozen out of their solutions. A colloid does not lower the freezing point of the liquid containing it, but as the liquid freezes it collects in the remaining liquid portion until it has no further retreat. That is why all packages of vat dye pastes are marked "Keep from Freezing." A frozen vat dye is a watery mess containing hard pellets of the coloring matter that can never be pasted again without special grinding or chemical treatment.

The most important colloid phenomena, which corresponds to the chemical property called affinity, is the property of colloids having opposite electric charges uniting with each other, adsorbing. These unions differ from chemical unions in that they are neither constant nor definite, although there seems to be a saturation point for both factors in the union. Every colloid possesses an electric charge, whether it is in liquid form, or is simply a dispersion of an

insoluble substance, or is a jell or is a solid insoluble substance of colloid nature.

After many years of argument it is now admitted by all that the operations of ordinary dyeing are simply colloid adsorptions. The dyestuff having an opposite electric charge from the fiber is drawn and affixed to the fiber, the exhaustion of the bath being assisted by the salts added, in the case of substantive cotton dyes, but in the case of acid wool dyes the added acid sets free the color acid, which has so strong an attraction for the fiber that the dyeing is very rapid and uneven until we add some Glauber's Salt, which exerts what is called a buffer action and restrains the action of the acid. In the same manner the old dyers were fond of adding to an acid dye some dyewood extract, such as Archil, Cudbear, Fustic, Hypernic, etc., without knowing why such addition always gave more even dyeings than the acid dyes alone. A too rapid dyeing color may always be restrained by the addition of some colloidal material. These materials may act by obstructing traffic, as it were, and preventing a free diffusion of the dyebath ingredients. Levelling agents generally depend for their efficiency on this sort of effect. Old wool dyers would start the day with the light shades and dye each succeeding lot in the exhausted bath of the former, claiming that such a procedure gave them better penetration and levelling, which of course was due to the gradual accumulation of extractive matters from the fibers themselves.

Dyers of logwood black on silk use a basic sulphate of iron as a prepare; this is diluted short of the point where a heavy precipitate would form and so contains colloidal ferric hydroxide, which absorbs readily with the silk fiber and is held until further washing and soaping actually forms a true precipitate of it.

These few examples simply indicate the part played by the colloid state of matter in the practice of dyeing; we might go on and cite hundreds of instances which could be better explained on a basis of colloids than by orthodox chemistry. The dyer's problems have been fairly well solved for him and whether his operations proceed by one theory or another is not so important as the fact that he is able to match his shades evenly in the shortest time. The textile printer worried little about colloids until he had to print vat dyes and now both he and the makers of vat dyes have become colloid conscious.

I was present at a test of the first American-made vat dyes and noted that very unsatisfactory shades were produced, although the dyes themselves were practically 100 per cent pure, and that was the whole trouble. When the dyes re-oxidized they tended to form microscopic crystals and so dulled the shades, while the pre-war foreign types had in them a colloid substance that prevented this re-crystallization and gave an amorphous film on the fibers and produced a full bright shade. At first the insoluble vat dyes were made into fine pastes by strictly chemical methods but now colloid mills are depended on to bring about the final degree of dispersion, so we may obtain pastes containing about 20 per cent of solid matter that will remain in suspension and show no coarse particles, but! we are dealing with colloid dispersions and we have to expect them to behave like colloids in every respect. Tried and proven dispersing mediums are used to promote stability but certain conditions may act to upset our best laid plans. Just as that natural dispersion, butter fat in casein, which we call milk, may allow its fat content to concentrate at the top of the bottle and upon agitation in a churn, may separate a lump of butter, just so may a perfectly dispersed vat dye encounter conditions that will result in the fine particles gathering together into small lumps and pellets and making it impossible to use as a printing color.

One common condition is the following: printers use British Gum as a thickening for their pastes, but British Gum is never 100 per cent Dextrine, it contains much unchanged starch and starch has a habit of boiling to a smooth paste when cooked with the full amount of water, but if cooked with a half amount of water and then diluted it can never be beaten or stirred to an absolutely homogeneous paste. It may look smooth and feel smooth but it is a more or less granular mess. The vat dye dispersion has an electric charge which makes it ready to unite with cellulose and as starch is closely related to cellulose chemically, the dyestuff is drawn to the masses of starch particles and so loses its fine dispersion at once. The resulting print is specky and the maker of the dye is censured. There are two sorts of remedies, either run the dye with a little paste through a colloid mill just before using or else convert all the starch to a more soluble form by boiling the British Gum for at least an hour with the alkali used for printing. This will convert the starch to dextrine and finally to caramel and will repay the printer by not only giving a smoother print but by being more easily washed out after the printing. Now most printers do boil up their gum with the Potash, but not all watch the operation to see that they have really a starch-free paste when it is finished, with the result that when the dispersed vat dye is added each small globule of starch becomes coated with dye particles, which gives the same effect as when the dye itself is improperly dispersed. If the print shop is not equipped with colloid mills, the following precautions had better be taken: stir the dye paste first with the glycerine, then with water and a small amount of

thickening and thus satisfy the affinities of the colloid particles of the dye before mixing with the balance of the thickening. Such a procedure will generally give a smooth print but still a run through a mill is preferable.

Any dyer, printer or finisher will find it very profitable to make a study of his various materials from the standpoint of their properties as colloids, noting that their properties are not so much dependent on the chemistry of reactions as they are on the physical chemistry called colloid chemistry. The whole subject has been touched on but lightly for it is a vast subject and daily we are noting that it encompasses almost every detail of our lives and work. It is of far more importance for a worker in dyes to know how the colloidal state of matter may be expected to behave than it is for him to know that Sulphuric Acid is H_2SO_4.

It may be interesting to discuss the simpler methods we use to recognize the state of colloid dispersion. Mention has already been made of the spotting of a colored solution on filter paper and of noting whether the color on the reverse side is of the same intensity as the top side; if this is the case and the right side is free from all traces of sediment or precipitate, we may assume that the dispersion is good, the ring of pure water showing us that we are dealing with a colloid and not a true solution.

The usual laboratory practice of making a dilution with water and observing the time of settling of tall cylinders as a method of comparing the relative value of vat dye pastes is open to many objections as the great dilution will introduce many elements that will favor the flocculation of the dispersed dye and so give results that may be misleading. Colloids without color are recognizable by several well defined properties; a solution, or as they are properly called sols or dispersions, may be perfectly clear and transparent but when a ray of light is directed through them they appear more or less cloudy or translucent, just as a ray of sunlight entering a room seems clouded by the dust particles in the air. Further, all sols acquire the faculty of easily forming a foam when agitated and when any liquid shows a disposition to foam it may be attributed at once to the colloids present. Many means have been devised to prevent this undesirable foaming, generally based on the property of certain liquids to lower the surface tension of the water. Turpentine, Fusel oil, various Glycols, Pyridine or Alcohol are used commercially.

Occasionally in printing the well dispersed color seems to acquire a strong affinity for the smooth portions of the copper rolls and will cause a smear that the doctor blades cannot scrape off; in such cases it is customary to add a small amount of stainless mineral oil to the paste, which being well dispersed in the mass, has a still greater affinity for the copper and permits the printing color to be readily removed from the copper by both fabric and doctor blade.

Naturally, this short paper cannot cover all phases of such a widespread subject so we trust that if there are any personal problems you will present them for discussion by the meeting at large.

Chairman Gaede: Are there any questions that anyone would like to ask Dr. Pierce? I am sure there are some questions that some would like to have cleared up on the more practical side.

Are there any printers here who would like to ask some questions?

Is there anyone who wishes to ask Dr. Travis any further questions on his paper?

Mr. Springer: There is one question I would like to ask as regards printing pastes. I have noticed when making up a printing paste, for example, when it is hot it gives a perfectly clear paste. Apparently it is in solution. Then on cooling it seems to cloud up somewhat. As far as I can see, it seems as if it is going into a colloidal state and the particles have become larger than they were originally. When spotted on glass, no noticeable particles are seen and when printed it gives a satisfactory print.

Will this paste give as good a print as it would give if the paste were perfectly clear? That is, will it be as fast and as full and as bright, or is there a definite ruling as regards this clouding?

Dr. Pierce: First, let me ask, what class of dyestuffs are you referring to?

Mr. Springer: Let's take Acid colors.

Dr. Pierce: The Acid colors should give you a clear paste if you use a full concentrated color and don't use it in too great a quantity. If you have used so much color that you have a super-saturation there, it will get cloudy.

Then, what kind of gum thickening are you using? Is that transparent?

Mr. Springer: The ordinary kind.

Dr. Pierce: It should remain transparent.

Mr. Springer: Here is a case where it happened.

I use a dyestuff known as Acid Brown Supra G and it is very insoluble in water. I brought it into fairly good solution by using Resorcin, and that seemed to give me a fairly good paste. Then, when cooling, I got this noticeable clouding, and when stirring it leaves a mark of the stirring rod, which is very characteristic of that type of paste. Still, when I printed it, it showed a satisfactory print.

Dr. Pierce: Do you know whether that Brown has a Schultz number or colour index number?

Mr. Springer: I don't.

Dr. Pierce: Nor do I. It may be a mixture and of course we can't tell you much about that. It is probably a mixture of an Orange.

Mr. Springer: Is there no definite statement that can be made regarding that type of paste?

Dr. Pierce: All that we see as a rule are clear if they are not overloaded with color. There is no reason why the color should be precipitated out unless there is a lot of Glauber's salt present.

Mr. Springer: After all, they are more soluble in hot solutions than cold.

Dr. Pierce: They are.

Mr. Springer: Suppose this takes place in a solution cooling; that is, when it is hot it is perfectly clear and on cooling it tends to cloud.

Dr. Pierce: If you get a good print from it when it is in the steamer it will go into solution again, so no harm is done.

Mr. Springer: In other words, the steamer tends to fix it as though it were in true solution?

Dr. Pierce: Yes, it would fix part of it, then it would go into solution; then it would fix some more until the paste had been exhausted of color.

Mr. Clemens F. Hoppe: Do you mean to say that the steaming would bring that particular color into solution?

Dr. Pierce: It would utilize, first, what was in immediate contact with the fiber and fix that; then some more would be available, and some more. It would take it up, as from a reserve supply that was there.

Mr. Hoppe: I have noticed that particularly with a half ounce per gallon of Chrysophenine Yellow.

Dr. Pierce: Which is a very insoluble yellow.

Mr. Hoppe: In hot solution it seems to be in perfect solution but as it cools you have a mass there that will just about print, and it prints evenly. We have no trouble with speckiness, and after steaming the color is uniform.

You say that is due entirely to the steaming, that the color is even afterwards?

Dr. Pierce: Yes. Whatever is in excess is taken up as from a reserve supply as it exhausts. The print paste exhausts just the same way as a dye bath exhausts until finally all the color is taken away from the gum.

Mr. Hoppe: I don't understand that yet. A half ounce per gallon Chrysophenine Yellow is adsorbed by the fiber, is it not?

Dr. Pierce: During the steaming; not until you do steam.

Mr. Hoppe: That is, during the steaming process your fiber exhausts the dyestuff from the gum?

Dr. Pierce: Yes, just the same as piece goods would exhaust dye from a dye bath. It is in more intimate contact than it is in the dye bath, but an actual exhaustion takes place.

Mr. Hoppe: In other words, a separation takes place in the steaming where the dyestuff is separated and goes to the fiber?

Dr. Pierce: Yes.

Mr. Hoppe: Dr. Pierce, would you say that was characteristic of most of the Direct dyestuffs, or not? I have noticed it with several.

Dr. Pierce: There are not many that have the insolubility of Chrysophenine. The majority are much better than that. But of course it is possible to select a series of very soluble ones, if you look for them. The higher concentrations are always more soluble than the weaker ones.

Chairman Gaede: Are there further questions?

Well, I am sure that everyone is pleased to have heard these two phases of colloid chemistry. The two papers which have been presented tonight fit in very well together. Perhaps there are other questions.

We are certainly very fortunate in having had colloid chemistry explained to us so well this evening and I would like to ask for a rising vote of thanks to Mr. Travis and Dr. Pierce.

A rising vote of thanks was extended to Mr. Travis and Dr. Pierce. (Applause)

Chairman Gaede: If there is no further business, the meeting will stand adjourned.

The meeting thereupon adjourned at 9:35 o'clock.

AMERICAN DYESTUFF REPORTER

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LOUIS A. OLNEY
Professor of Chemistry and Dyeing, Lowell Textile Institute
Directing Editor

BLISS MORRIS JONES
Managing Editor

MYRON DREW REESER
Advertising Manager

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THE WORKING MAN AND MACHINERY

MORE than half of all textile machinery is obsolete—new machinery increases profits. How often we have heard these phrases in the last year! Without a doubt they are true, but the biggest plea of all on behalf of new machinery is entirely neglected. That is, that machinery is, in the long run, a distinct benefit to the working class.

For a number of years past the laborer has looked upon the machine as an ogre, or a devastating metal dragon—ruthlessly devouring jobs, turning men into robots, breeding callous efficiency. Is it that—or is it a job creator, a social benefactor and a potent business stimulator?

A great majority of clear-thinking students of the subject see the machine creating wealth, and not for the owners alone. They recognize its prime responsibility for the rise of giant industries concerned with a vast array of conveniences and comforts. They look upon it as the source of unprecedented wage scales, as the liberator of the working man from the age-old burden of back breaking labor.

The skeptic will say this is all right for the man who keeps his job and tends the machine, but he wants to know what happens to the man or men who have been displaced by the machine. These men must go through a period of rather difficult readjustment. However, in the end their work in life will be made easier by the machines. Mr. Franklyn Hobbs, director of research in an Illinois financial institution, states that "it is an unassailable, incontrovertible fact" that the introduction of automatic and labor-saving tools and appliances into the manufacturing industry has not reduced the amount of money paid by that industry to labor and has not displaced workers in certain industries as rapidly as avenues of employment have been opened up to them in other industries.

Thus we see that up to now the introduction of new machinery has resulted principally in a readjustment of labor. In addition, it has decreased the average working day. This last fact is bound to prove more and more important.

When we stop to think of the average laborer's life, we shake our heads. He works anywhere from eight to twelve hours a day. His opportunities for recreation and improvement of mind are almost nil. What then will improve his situation?

Let us just do a bit of supposing. Supposing machines are invented to do almost anything better and better, and quicker and quicker. Supposing that prices hold the same level, wages and hours of labor stay the same. What would be the result? There is only one answer. The manufacturers would make fabulous fortunes and half the world would be unemployed. However, no such situation could come, for with half the men unemployed the market for goods would be too small. The answer then is to increase machinery, maintain wages, and cut the hours of labor. Under such a system the manufacturers would make as much as ever, the laborer would earn the same as before, and his hours of toil would be reduced considerably. He would have time to enjoy life. He could have recreation and time to improve mentally. In other words, he would be able to lead a life worth living.

This trend has already been felt. We have only to check up on statistics for a number of years back to see how the working day has been shortened because of the introduction of machinery.

It doesn't seem beyond reason to believe that some day we will reach a super-machine age when men can only work three or four hours a day if they are all to be employed. Some might consider that a real machine age, but to call it the laborer's age would be more nearly correct, for the machines would be truly working for the laborer.

Every advance in the industrial age has created hardships for many, but has in the end benefited everyone. It will always continue to be so, and year by year conditions will continue to get better and better for the working man.

MEDAL FOR DISTINGUISHED SERVICE

ON March 24, the occasion of the 76th birthday of Andrew W. Mellon, the American Institute of Chemists announced the award of its medal jointly to Andrew W. Mellon and Richard B. Mellon for distinguished service to the science and profession of chemistry.

Dr. Frederick E. Breithut, President of the American Institute of Chemists and head of the Department of Chemistry at the Brooklyn College, in making the announcement, said:

"The Institute medal is awarded annually for distinguished and outstanding services to the science and profession of chemistry. Andrew W. Mellon and Richard B. Mellon have contributed to the advancement of chemistry in its broadest aspects and have fostered the progress of industry by their far-seeing and unselfish efforts. Through the agency of the Mellon Institute of Industrial Research they have been leaders in the great forward march of the American chemical industry.

"The Mellon Institute has made not only great industrial discoveries which have created new industries and strengthened old ones, but has also provided a body of trained scientific investigators who have contributed towards consolidating America's position in the scientific and technical world. The Mellon Institute is the West Point of our industrial system, assisting the United States to attain and hold its foremost position amongst the industrial nations of the world.

"The Mellon brothers in making this program possible have contributed to the advancement of science and technology, have made it possible for the profession of chemistry to rise to its powerful position in our industrial system and have given chemists numberless opportunities to serve the country and to secure professional advancement.

"In 1911 the late Dr. Robert Kennedy Duncan of the University of Pittsburgh inaugurated his now famous research procedure—the industrial fellowship system—in the department of industrial research at the University. Andrew W. Mellon and Richard B. Mellon noted the practical success of this educational experiment and saw the soundness of the method of benefiting American industry as a whole by studying manufacturing problems under suitable conditions and by training young scientists for technical service.

"As a result of this interest they founded the Mellon Institute of Industrial Research in March, 1913, and placed the industrial fellowship system on a permanent basis. The institution was incorporated in 1927 and its affairs are managed by its own Board of Directors of which the Mellon brothers are members. Their continued financial support has made it possible to develop the industrial fellowship system to its present strong position in science and technology.

"The activities of the Institute have assisted in bringing to the United States the largest chemical industry in the world and have led not only to the training of a large number of young scientists and technicians, but also to the creation of new industries.

"Men of large means and grand vision are needed to bridge the gap between uncommercial scientific speculation and commercial reality. Andrew W. Mellon and Richard B. Mellon have proved themselves to be this sturdy bridge. What they have done has become more or less a part of our industrial fabric and technological organization, but it required great vision and courage to see this twenty years ago when research was still merely an unwelcome step-child in most of our industries."

Textiles in the Amended Design Copyright Bill

By Waldon Fawcett

IF Congressional authority is to vouchsafe to American industry, on the installment plan rather than in full scope, the coveted system of Design Copyright, the limitation may influence the favorable reaction that has been anticipated by the dyestuffs community. That is, assuming that design protection in its fullest measure should prove, indirectly if not directly, a stimulant to the consumption of coloring materials. Considered in this light the potentialities of Design Copyright, Limited, must be appraised separately so long as an influential group in the U. S. Senate is committed to the idea of a progressive program of design registration in lieu of design patent.

Restriction in the scope of Design Copyright, as proposed by the Senate Patent Committee when it revised the Vestal Bill, after its passage in the House of Representatives, is of concern, principally, to dyestuffs interests because of the interpretation which shall be placed upon the term "textiles." The phraseology submitted to the 71st Congress, late in its final session, was none too explicit. The Senate edition, as submitted by Senator Hebert, enumerated five classes of manufactured products to which Design Copyright was to apply in the beginning. The five classes, in the order of their designation, comprised textiles, furniture, lamps and lighting fixtures, shoes or other footwear, and jewelry or articles manufactured from precious metals.

In the case of "textiles" alone was there any elaboration of the specification. In that instance, the full notation read: "Textiles, lace and embroideries of all kinds whether the designs are woven into or applied to the surface of, or incorporated into the substance or fibers of the fabric." This stipulation is obviously sufficient to encompass all textiles regardless of how the designs be executed or the color translated. What is left to be desired is information on the explicit range and application to be given the term "textiles."

Should it ever be necessary for the Register of Copyrights to give effect to legislation along these lines, that official, finding no detailed guidance in the statute phrased as above quoted, would have to follow the common practice of ascertaining the intent of Congress with respect to obscure expressions. By tradition, the approved source of information to clarify language of doubtful meaning is the Congressional Committee which drafted or redrafted the measure—in this instance, the Senate Committee on Patents, which inserted the zoning plan whereby design protection would be rationed to only five commodity classes.

If the confidential records of the Committee are consulted there will be no difficulty in ascertaining that it was the intention of the majority of the Committee to

open the Copyright only to textiles in primary marketable state rather than to garments or other products manufactured from textiles. The term "fabric," found at the close of the textile specification, gives the clue to what was in the minds of the Senators. The REPORTER has information from an authoritative source that it was not the intention to have the term "textiles" extend to wearing apparel, to draperies, rugs, carpets, nor floor coverings.

This arbitrary separation of manufactured products that seem to have much in common will be the better understood by taking into account the process followed by the Senate in editing a measure which had suddenly taken on a controversial aspect unrevealed in the House of Representatives. Without formally confessing so much, the Senate Committee followed the policy of attempting to give relief to the industries which had protested that their very existence was threatened by the spread of design piracy. And, by reversal of this formula, Design Copyright was withheld from the industries that, by their silence, indicated their satisfaction with the existing Design Patent system or, by means of representations direct to the Committee indicated an active opposition to the proposed expansion of the Copyright structure to cover original, ornamental and artistic designs in industry.

This technique on the part of the Senate Committee explains, for example, the exclusion of floor coverings from the tabloid edition of Design Copyright. In January, there appeared before the Committee, among other voluntary witnesses, Mr. William Sutherland of the Bigelow-Sanford Company to voice a protest on behalf of "probably the biggest domestic manufacturers of floor coverings in the United States." Mr. Sutherland gave lip service, as have most of the other opponents of Design Copyright, to the principle of protection of design. But he demurred at universal design copyright legislation with the misgiving: "We feel that it will meet with a tremendous lot of litigation, because of proving our rights to designs and adaptations."

The Bigelow-Sanford representative, who predicted that under Design Copyright his company would have to register 1,500 designs a year, supported the position which has been taken by Mr. Charles W. Johnson, President of the Botany Worsted Company. Mr. Johnson, who claims that his mills at Passaic and Garfield, N. J., spend from $300,000 to $500,000 a year on its organization for designing, insists that his firm wants a protective bill put through. But he held that the Vestal Bill, as passed by the House, did not properly protect the manufacturer. Conceding that "all through this country the manufacturers realize the damage that is being caused in their creative program," Mr. Johnson was worried by the possibility that Design Copyright would hurt more than it would help.

Criticism and apprehension such as this impelled the Senate Committee to devise the plan it finally recommended—a device that would put the principle of Design Copyright to the practical everyday test but would leave it to experience to demonstrate that the Copyright should blanket the entire field of manufacture. Just here it might be added, in explanation of the attitude in the Senate, that the Chairman of the Senate Committee has all along held the opinion that the institution of Design Copyright, if authorized, would not have the wide utilization that has been predicted for it, on the basis of the number of original designs produced annually in American industry. The Chairman of the Senate Committee had the impression that only a small proportion of the original designs in the textile industry are pirated and on that premise he has theorized that only a modest number of test cases would be brought in court to vindicate copyrighted designs. If that be so, a partial establishment of Design Copyright would suffice as well as an unlimited one for try-out and demonstrational purposes.

There is no reason to expect that the compromise of Design Copyright, Limited, will be satisfactory to objectors such as the National Association of Retail Clothiers and Furnishers, even though studied effort be made to dodge the style and fashion elements in made-up garments by restriction to textile yardage, etc. Answering a question on behalf of the AMERICAN DYESTUFF REPORTER, Mr. Isaac Lande, General Counsel for the National Retail Dry Goods Association, said: "I am certain that the main objections of the retailers to the proposed legislation have not been obviated by the amendments proposed by the Senate Committee." He added: "I am in accord with the views expressed by Senator Dill that the restriction of the provisions of the bill to a limited class of articles serves only to increase doubt as to its constitutionality."

In official circles at Washington a feeling has grown up, these past few weeks, that the best antidote for design piracy may lie entirely outside the sphere of both patents and copyrights. This in response to the dread voiced by Mr. Johnson and other members of the textile industry that the Copyright cure might be worse than the disease. The alternative which has caught the imagination of a few law-makers, who have been much in conference with textile tradesmen, is the trade mark. With a record before them of the success of the "Imperator" coating, running to 26,000 pieces in 1930, the onlookers at the Capitol have asked why textile tradesmen in need of protection could not fortify themselves in part at least by a use or registrable varietal names. The question was put, for one, to Mr. Sutherland of the Bigelow-Sanford Company, who replied that his company had never made any attempt to use the trade mark method.

Dyeing Assistant for Indigosols

Under the name of Indigosol Soap S P, the Carbic Color and Chemical Company have introduced a special assistant for dyeing Indigosols on wool. This new product is said to do away with many troublesome operations which were formerly used to obtain fastness to rubbing.

Wool Oils

(Continued from page 196)

To the average purchaser of wool oil the practical test of emulsification is of the highest value as it gives an index to the stability of the product and the facility with which the oil will scour. As the emulsified oil in question usually stands under observation over an indefinite period of time it is also possible to gain a very good opinion of its behavior towards gumminess (this is not the usual procedure for checking the gumminess of an oil but it has more definitely a practical value than when the unemulsified oil is tested). The tendency, if any, to rancidity can also be detected readily in an emulsion of long standing.

The error entering into such a test when carried out in the mill office, as it many times is done, is the unknown factor of free fatty acid content, the value of which is important if a well balanced condition of emulsion with alkali is to be made. A haphazard quantity of alkali added to an unmeasured amount of water to which is added the oil without consideration for proportions in relationship to the free fatty acid present in the fatty oil of the mixture cannot be expected to give a true picture of the emulsification of the product under examination, nor can any of the characteristics of this emulsion be taken as reliable data for the oil in question. It is well to carefully measure the volume of water and of oil to be added. And, of course, the chemist will be in possession of data from his analysis that should give him the means at hand to make a very well balanced emulsion or at least one as well balanced as the components of the mixture permit.

It is possible to gain a very clear conception of the product by dropping one single drop of the oil into a large volume of water, previously made slightly alkaline with borax or soda, and watching its dispersion. Some products will enter into an emulsified state and so disperse through the water as readily as milk and will leave no oily film at the surface, while other products may emulsify but slightly or not at all. Any product which will disperse through the water approximately as does milk will never cause any annoyance in scouring and if its other characteristics prove satisfactory, as they generally do, such an oil will prove entirely satisfactory for use. On the other hand any oil that is difficultly "soluble" can be viewed with suspicion at the start.

Preliminary examination of an oil carefully carried out will often shed a great deal of light upon the practical value of the oil and save much tiresome analytical work on the part of the chemist, and in those plants where there is no chemist in charge it will eliminate from actual trial in the works many of the products which, if entered, would be found unsuitable.

It is true that many mills still retain their preference for "the fatty oils" as wool lubricants. Olive Oil, Lard Oil and Red Oil are widely used. These products, while used as wool oils, are not a part of the above discussion. They are purchased to certain specifications, either guaranteed or subject to analysis. They emulsify, as already pointed out, by reason of their free fatty acid content. Each of these named oils has some particularly advantageous characteristic beyond the basic matter of lubrication which to the user justifies his continued purchase of these high priced products. To some this advantage may be in the spinning of very low counts. To others it may mean nothing but a trade preference. Some hold they can secure brilliant white only through use of a fatty oil. But by far the greatest number use them because of their effect on fulling operations.

The fact is many full in the grease and there is of course a certain carry-over of soap building material from the fat oils or from mixtures high in fatty oils. For work of this kind it has proved much more economical and entirely as satisfactory to use a reasonably high percentage of fatty oil in a blend (with mineral oil) as to use the fatty oil alone. In fact, the finish of most goods is clearer and less heavy when using the blend. Or as the chemist will find by an extraction test his permitted residue will consist more of oil when using the blend and more of soap when using the fatty oil alone. And many times this soap residue is the cause of great loss to the mills in musty goods, or dead, lifeless stock, etc.

Another type of product has within recent years been widely employed as a wool lubricant. This is a mineral oil blended with some product capable of effecting the complete emulsification of the mineral oil portion. These as a general class are known as Soluble Oils. They form an immediate and complete emulsion when placed in water without the addition of any alkali. The first products of this type appeared years ago and will be sometimes met with today. They are prepared from the blending of fatty oils with a mineral oil and an alkaline soap in balance. When added to water they emulsify immediately and have certain advantages in waters of unknown hardness. They can be analyzed and checked as fatty oil blends.

Later a "base" of sulphonated oil was used to effect this emulsification of the mineral content of the mixture. Some of these products are highly efficient as wool oils. Their evaluation from a point of use as a wool oil is to be derived almost wholly from emulsification tests. There is no particular advantage in a complete chemical analysis beyond having a definite knowledge of their make-up and a check to see that they are not rosin filled or alcoholic. And as in most instances the alcohol, if present, is used to effect a balance between the base and the mineral oil and has no importance once the emulsion is made, this also is more or less an academic procedure. Because of the difficulty in controlling sulphonation, troubles have occurred in the use of the finish product, but this is more likely to take place in the "superfatted products," i. e., when a proportion of fatty oil is added to a Soluble Oil it is termed as "superfatted." This is done to improve the oiliness or to increase the fulling capacity of the product.

The napthenic sulpho acids from the spent lyes of refining oil have more recently found large use as "bases" for Soluble Oils. These products become, at once, very dependable as wool lubricants, as they are highly emulsifiable, very stable and free from any tendency toward rancidity. They scour with the greatest of ease. Combined with the proper mineral oil they are among the most satisfactory and at the same time low priced products at the disposal of the textile mill for stock lubrication. From a practical consideration they are best checked through emulsification tests. Chemical analyses of Soluble Oils, be it borne in mind, are not comparable with the analyses of the Fatty Oil Blends. By example, 78% mineral oil in a fatty oil blend might be entirely valueless as a wool oiling product, whereas, a similar mineral content in a Soluble Oil not only might be, but probably would prove highly satisfactory from all points of practical consideration.

In summary, we have in the problem of wool oiling two vital considerations ever present—the positive lubrication of the stock and finally the complete removal of the lubricant by means economically sound. Other justifiable considerations may influence the preference for any certain product but the aforementioned considerations are basic. The wool oils used by the mills today fall into one of the following classes or types of product:

1. Fatty Oils—Emulsion by alkali.
   a. Olive Oil.
   b. Lard Oil.
   c. Red Oil (Elaine).
   d. Peanut Oil.
   e. Other vegetable or fatty oils or combinations thereof.
2. Fatty Oil Blends—Emulsion by alkali.
   Combinations of various kinds of fatty oils, in varying grades and proportions with mineral oils.
3. Self-emulsifying Fatty Oil Blends.
   Combinations of fatty oils with mineral oils together with the addition of an alkaline soap in balance. No alkali need be added to bring about emulsification.
4. Oil Soaps.
   Combinations of fatty oils with mineral oil and a fatty oil soap. Appear in form of syrup like liquids or gels. Emulsify directly upon addition to water.
5. Sulphonated Oil Bases in Blends.
   Various sulphonated oil products combined with mineral oil to make a stable, balanced emulsion upon addition to water without alkali.
6. Napthenic Bases in Blends.
   Carefully prepared bases from napthenic sulpho acids in combination with mineral oils. Form emulsions upon addition to either hot or cold water.

Note: Those unfamiliar with and wishing detailed analytical procedure for oil determinations are referred to "Oil Analysis" by Augustus H. Gill; "Organic Analysis" by Henry C. Sherman or other similarly reliable texts.

New Pinking Scissors

Perfection of a method for Pinking silks, cottons, woolens, shirtings, and in fact all kinds of textiles, leather, oilcloths, felts, etc., is announced by the Progress Pinking Scissors Co., Inc., of 158 Greene Street, New York City, of which Samuel Briskman is president.

The new method of Cutting and Pinking in one operation is the result of years of experimental work carried on with the view of creating a scissors that will greatly facilitate manufacturers, cutters, wholesalers and retailers in Pinking cloths and fabrics of all kinds.

In perfecting the present tool, Mr. Briskman pointed out it has been the aim of the company to save time, labor and effort that is usually necessitated in carrying of fabric bolts to the Pinking Machine, which has heretofore remained stationary in a certain fixed spot.

The newly developed Pinking Scissors may be easily carried by an employee to any part of the establishment. They also eliminate the double work of cutting the cloth and then Pinking it by the method used in the past. This is now done in one operation with the Progress Pinking Scissors. A very great advantage in cutting swatches is among other of its many functions.

Mill Men Invited to Hear Loom Expert

Mr. Albert Palmer, head of the Research Department of Crompton and Knowles Loom Works, Worcester, Mass., will deliver a series of lectures at the State College Textile School, Raleigh, N. C., on Monday, April 13.

The subject matter of the lectures will be grouped under four heads:

(1) Costs and their relationship to loom operation;
(2) The application of time study methods to the weave room;
(3) The design and operating characteristics of modern weaving machinery;
(4) Some fundamental principles of loom engineering.

Mr. Palmer is an expert in his line and his lectures will be very interesting to textile students and mill men. The lectures will be open to the public and Dean Thomas Nelson announces that a cordial invitation is extended to all who are interested in the textile industry to visit Raleigh on April 13 and hear Mr. Palmer.

New Finishing Product

General Dyestuff Corporation recently announced a new sizing and finishing product manufactured by the I. G. Farbenindustrie Aktiengesellschaft under the name of Vinarol A for Rayon and Silk Hosiery.

It is said to form an efficient protective coating, hold the filaments together and increase tensile strength without sacrificing flexibility or smoothness. It is easily and quickly prepared, easily washed out in hot water and it is not necessary to wash out sizing if the material is to be dyed. I. G.-305.

Appoint Chemical Dinner Committee

Fred A. Koch, Dow Chemical Co., President of the Salesmen's Association of the American Chemical Industry, has announced the appointment of the special committee to have charge of the Chemical Show Week Dinner, sponsored by the organization during the week of each Chemical Exposition. Ira Vandewater, R. W. Greef & Co., will be chairman; William Haynes, Chemical Markets, is in charge of securing speakers; B. J. Gogarty, American Solvents & Chemicals Corp., invitations; Grant A. Dorland, MacNair-Dorland Co., publicity; Victor E. Williams, Monsanto Chemical Works, hotel and menu; Robert L. Wilson, Dow Chemical Co., tickets and seating list, and Charles F. Roth, representing the management of the Chemical Show.

The dinner has been scheduled for May 7. It will probably be held at the Roosevelt Hotel. As usual, the principal speaker will be a prominent individual whom it will be worth while to hear. This dinner attracts a larger gathering than any other in the chemical field. Around twenty of the industry's most active associations, including most of the technical organizations, will cooperate with the Salesmen's Association in urging all of their members and friends to attend this regular feature of Chemical Show Week.

New Waterproofing Process

The Sandoz Chemical Works have introduced a new waterproofing process which they claim does not detract from the naturally soft handle of the fabric under treatment.

Unlike the older methods which necessitated the use of two baths, the new Cerol Process achieves the desired result in one bath. The resultant proof is said to more than equal the best obtained by any of the old two bath methods, and the handle is claimed to be much superior.

Mr. Sylvester Kaas has become associated with the Atlas Refinery of Newark, N. J., as Technical Director of the Textile Oil Division. Mr. Kaas has been identified with the textile oil industry for a number of years through his work with the National Oil Products Company and as Plant Manager of the Textile Oil Division of John Campbell & Company.

New Testing Laboratory

Adolph J. Winkler, consulting textile specialist and textile chemist, recently established a testing laboratory at 40 Worth Street, New York City.

The laboratory is equipped to make tests of both a physical and chemical nature on yarns and fabrics. Such defects as uneven dyeing, tender cloth, degree of bleach and mercerization and improper oiling are typical of the problems handled.

Mr. Winkler is a graduate chemist with post-graduate work at the leading textile schools of the country. He has had more than twenty years' experience in the mill and has been connected with physical investigations and research in the laboratory.

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

PRINTER

Chemist-Colorist, 35 years of age, married, last 6 years Supervisor of Printing Establishment of one of the largest Eastern Plush Mills. Experienced in the printing of all colors on Mohair, Silk, Rayon and Cotton Plushes, also Brocaded Velvets and Soda Prints. Some Laboratory, Dyeing and Finishing experience. Will locate anywhere. Address: Classified Box No. 654, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

POSITION WANTED

Secretary-Stenographer—8 years' experience with importing and domestic Chemical and Dyestuff manufacturing concern, desires a position in similar capacity wherein excellent knowledge of sales operations may be of service. Address: Classified Box No. 668, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

POSITION WANTED

Executive Chemist—German graduate; fifteen years' experience intermediates, Dyestuffs, etheric oils, former executive abroad; five years with American dyestuff corporation, wishes position as research and plant chemist or technical adviser to executive. Would consider temporary connection for special research problems. Address: Classified Box No. 669, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.